USING STABLE ISOTOPES TO DEVELOP A REGIONAL HYDROGEOLOGICAL MODEL AND CHARACTERIZE NITRATE SOURCES IN GROUNDWATER

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ABSTRACT

Semi-arid regions, like the Okanagan Basin of British Columbia, Canada, are often faced with the difficulty of managing limited groundwater and surface water resources while accommodating rapid population growth and increasing land development. In the South Okanagan Basin, a better understanding of groundwater recharge sources, groundwater availability and susceptibility of water supplies to anthropogenic contamination is needed to best direct and protect the region's water resources. The purpose of this study was: (1) to characterize the regional hydrogeological setting of the South Okanagan Basin by establishing an isotopic and geochemical framework that included precipitation and surface waters of the Okanagan Basin and groundwaters of the South Okanagan Basin; and (2) to characterize nitrate contamination and its sources in shallow groundwaters of the Osoyoos area. Stable isotopes of water, nitrate and dissolved oxygen, groundwater chemistry, water levels and enriched tritium, tritium/helium and/or radiocarbon age dating techniques were used. Two provisional local meteoric water lines were established for the Okanagan Basin: $\delta^2H=6.06\delta^{18}O–31.21$ (Osoyoos) and $\delta^2H=7.03\delta^{18}O-12.68$ (West Kelowna). Surface waters of the Okanagan River system were sources of irrigation water in the South Okanagan Basin valley and irrigation-return flow was the primary source of recharge for shallow groundwaters. Fractured bedrock in highlands east and west of the valley were not a significant source of recharge for shallow valley groundwater, however, may recharge deeper, or basal, valley deposits. As irrigation-return flow controls shallow groundwater dynamics in the valley sediments, groundwater quality is susceptible to anthropogenic contamination. In Osoyoos, nitrate was present in shallow groundwaters at concentrations of up to 24.4 mg/l N as a result of fertilizer nitrogen applied at the soil surface, mostly at orchards. Two agricultural drainage systems in north Osoyoos discharge roughly 1,900 kg N/year from nitrate-contaminated groundwater directly into Osoyoos Lake and may contribute in part to its eutrophication.

Key Words: isotopes, precipitation, surface water, regional hydrogeology, nitrate, groundwater, agricultural drainage, semi-arid

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CHAPTER 1
OVERVIEW AND OBJECTIVES

1.1 Introduction

The Okanagan Basin, located in the Southern Interior Plateau of British Columbia, Canada, has drawn a considerable amount of attention over the last few decades, not only in terms of its of rapid population growth and land development practices, but also because of its dependency on limited surface water and groundwater resources (Cohen et al., 2006). Along with the semi-arid climate, land use changes, and the potential for adverse effects due to climate change, management of these water resources is especially critical to ensure their quality and sustainability (Cohen and Kulkarni, 2001; Merritt et al., 2006; Neilsen et al., 2001).

The Okanagan Basin lies in a north-south trending valley and includes all lands surrounding streams and lakes that discharge into the Okanagan River (Figure 1.1). Within British Columbia, the Okanagan Basin extends for roughly 160 km, from Armstrong in the north to Osoyoos at the Canada-United States border in the south, and covers an area of roughly 8,200 km^2. The Basin extends for about 115 km south into the United States. The Okanagan River system is a major supplier of the Okanagan Basin's water needs, where up to 200 water licenses have been allocated along the Okanagan River for irrigation, waterworks, domestic, land improvement and storage purposes. As surface waters reach their allocation limits, an even greater reliance will be placed on the Basin's groundwater resources.

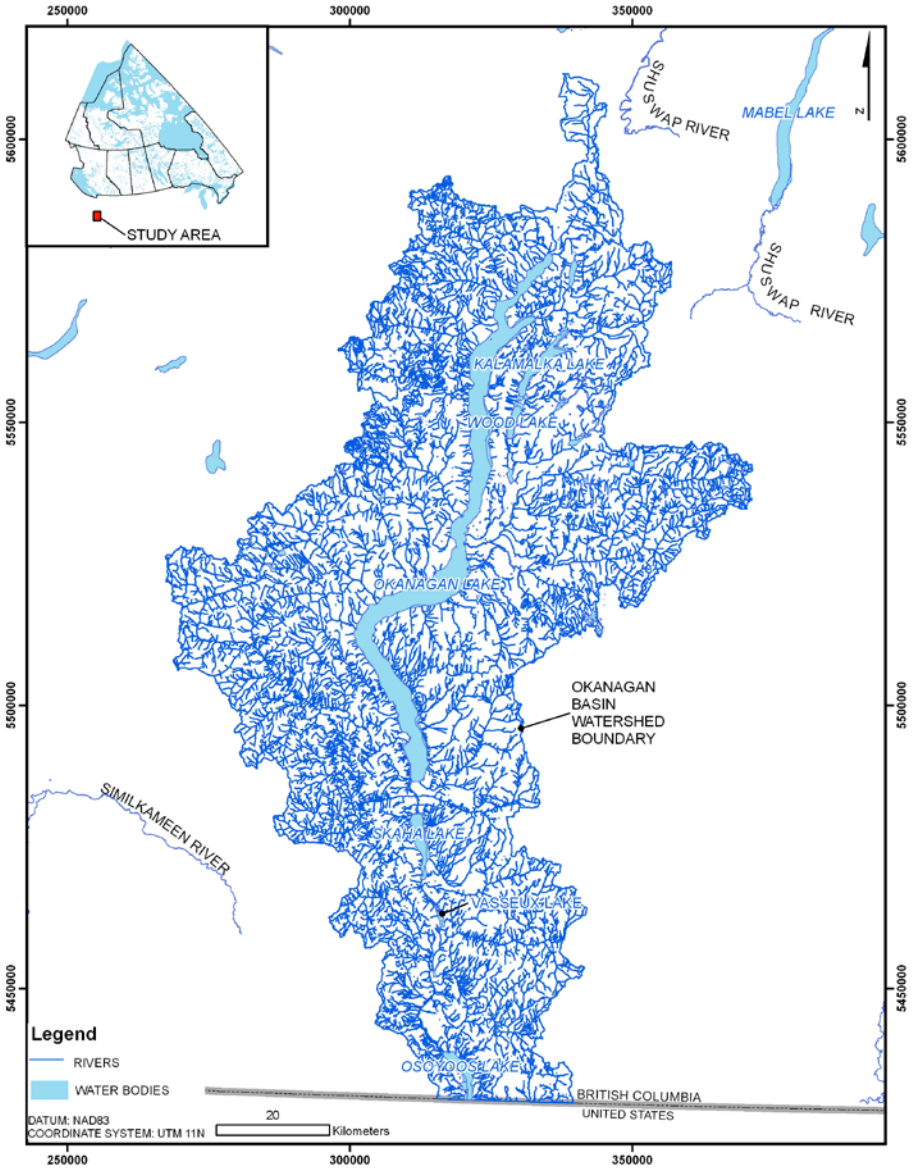

Figure 1.1. Location of the Okanagan Basin within British Columbia, Canada. Map produced using river data from the website www.geobase.ca (National Hydro Network, station 08nm001) and national boundary line and water body data from DMTI Spatial Inc.

This study is part of a larger research program currently being conducted in the Okanagan Basin. The study was completed over a three-year period and was funded by a research grant from the Canadian Centre of Excellence in Water. The study is a component of the on-going Canadian Water Network research project: *Assessment of Regional Water Resource Impacts from Agriculture*. This study is also part of the Groundwater Assessment of the

Okanagan Basin, a working group of the Okanagan Basin Water Board's Okanagan Basin Water Supply and Demand Project.

The overall objectives of this study are: (1) to characterize the regional hydrogeological setting of the South Okanagan Basin by establishing an isotopic and geochemical model that includes precipitation and surface waters of the Okanagan Basin and groundwaters of the South Okanagan Basin; and (2) to characterize contaminant sources (specifically, nitrate) in shallow groundwaters of the Osoyoos area. These objectives are reached using a multi-faceted approach – the coupling of geochemistry, stable isotope analysis (^{2}H and ^{18}O in water, ^{15}N and ^{18}O in nitrate, and ^{18}O in dissolved oxygen), water level measurements and enriched tritium (^{3}H), tritium/helium ($^{3}H/^{3}He$) and/or radiocarbon (^{14}C) age dating.

The methodology, results and conclusions of this study are presented in a manuscript-based thesis. Following this introduction (Chapter 1) and a literature review (Chapter 2), the first objective is achieved in three manuscripts: Chapters 3, 4 and 5. Chapter 3 discusses the isotopic composition of precipitation in the Okanagan Basin. In this chapter, the isotopic composition of precipitation samples collected in Kelowna and Osoyoos were used to define an isotopic framework with which the isotopic compositions of subsequent surface waters and groundwaters collected from the Basin can be compared. Chapter 4 discusses the isotopic composition of select surface waters in the Okanagan Basin, in particular, those along the Okanagan River system. This chapter also compares the isotopic composition of select surface waters in the highlands of the South Okanagan Basin. Following Chapter 4, the study then narrows its focus geographically to the South Okanagan Basin. Chapter 5 discusses the geochemistry, isotopic composition, water levels and/or age dates of groundwaters in the valley bottom, benchlands and highlands of the South Okanagan Basin in terms of recharge sources. Along with the results of

the previous two chapters, a conceptual hydrogeological model of the South Okanagan Basin is developed. Although Chapter 5 focuses on the south portion of the Basin, the methodologies used thus far can be directly applied to model the regional hydrogeological setting of other parts of the Basin. The second objective is achieved in Chapter 6. In view of the hydrogeological setting and recharge environments identified in the previous chapters, Chapter 6 characterizes the source(s) of nitrate contamination in groundwaters and agricultural drainage waters in the Osoyoos area. Agriculture, primarily fruit orchards and vineyards, is one of the major economic industries in the South Okanagan Basin (including Osoyoos). Agricultural practices, primarily the application of nitrogen-based fertilizers, have resulted in elevated levels of nitrate in groundwater. A Conclusion, Implications and Recommendations chapter (Chapter 7) completes this thesis.

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CHAPTER 2
LITERATURE REVIEW

2.1 Stable Isotopes of Water

Within the water molecule, there are two stable isotopes of hydrogen: ^{2}H and ^{1}H, and three stable isotopes of oxygen: ^{16}O, ^{17}O and ^{18}O. The stable isotopes of hydrogen and oxygen are measured as the ratio of the two most abundant isotopes of a given element (for oxygen, these are ^{16}O and ^{18}O) (Clark and Fritz, 1997). The isotopic compositions of a sample are reported relative to the Vienna Standard Mean Ocean Water (VSMOW) reference for both hydrogen and oxygen, and expressed in the delta per mil (δ(‰)) notation (Clark and Fritz, 1997):

$$\delta(‰) = [(R_{sample}/R_{standard}) - 1]\cdot 1000 \quad (2.1)$$

where, δ(‰) is the isotope ratio in delta units relative to a standard, and R_{sample} and $R_{standard}$ denote the $^{2}H/^{1}H$ or $^{18}O/^{16}O$ isotopic ratios in the sample and the reference material, respectively (Clark and Fritz, 1997).

2.1.1 $\delta^{2}H$-$\delta^{18}O$ Relationship in Precipitation

The relationship between ^{2}H and ^{18}O in fresh waters correlate well on a global scale (Craig, 1961). This relationship is described as the Global Meteoric Water Line (GMWL) and is expressed by the equation (Craig, 1961):

$$\delta^{2}H = 8\delta^{18}O + 10 \text{ Standard Mean Ocean Water (SMOW)} \quad (2.2)$$

The slope of 8 is a function of the ratio of the isotopic equilibrium fractionation factors for ^{2}H and ^{18}O at 25 °C during equilibrium condensation, where the ^{2}H enrichment in water is roughly 8 times greater than for ^{18}O (Clark and Fritz, 1997). The ratio of the isotopic equilibrium fractionation factors varies with the temperature of condensation, and, therefore, an increase in temperature results in a decrease in slope (Majoube, 1971). The intercept of 10 is generally a

function of the meteorological conditions that occur during non-equilibrium evaporation of the ocean surface where the precipitation originates (Clark and Fritz, 1997). Both the slope and intercept can be affected by secondary evaporation of the precipitate during rainfall. The GMWL is an average of many regional and local meteoric water lines (LMWL) that differ from the GMWL in slope and/or intercept as a result of different climatic and geographic factors (Clark and Fritz, 1997). The isotopic composition of precipitation is typically localized near the global meteoric water line (Gat, 1996) and seasonal variability results in winter precipitation that is strongly depleted relative to summer precipitation (Gibson et al., 2005). A more precise relationship between ^{2}H and ^{18}O was subsequently established by Rozanski et al. (1993) using long-term averages of $\delta^{2}H$ and $\delta^{18}O$ values measured in precipitation at meteorological stations of the Global Network of Isotopes in Precipitation (GNIP), jointly operated by the International Atomic Energy Agency (IAEA) and the World Meteorological Organization (WMO). This relationship is expressed by the equation (Rozanski et al., 1993):

$$\delta^{2}H = 8.17(\pm 0.07)\ \delta^{18}O + 11.27(\pm 0.65)\ (\text{VSMOW}) \tag{2.3}$$

Deuterium excess (d-excess) is a measure of the deviation of a given data point from a line with a slope of 8 going through VSMOW (Araguas-Araguas et al., 2000) and is defined by the equation (Dansgaard, 1964):

$$d = \delta^{2}H - 8\ \delta^{18}O \tag{2.4}$$

Excess deuterium is found in precipitation when humidity is less than 100% (Clark and Fritz, 1997). Globally, the d-excess value is approximately +10‰, as global atmospheric water vapour forms from seawater with an average humidity slightly greater than 85% and produces precipitation that is displaced from seawater by approximately +10‰ for $\delta^{2}H$ (Clark and Fritz, 1997). Regionally, d-excess values vary due to differences in meteorological conditions at the

source region of the vapour mass relative to that at which the precipitation is derived (Merlivat and Jouzel, 1979). These conditions "fix" the d-excess value so that it remains unaltered during the rainout process (Harvey, 2005), thereby, providing information on the climatic conditions at the oceanic source region (Araguas-Araguas et al., 2000). Low d-excess values can reflect high humidity in the source region. For example, low d-excess values for Victoria, British Columbia, Canada, reflect high humidity during formation of Pacific vapour masses (Fritz et al., 1987). High d-excess values can result from lower humidity in the source region (Clark and Fritz, 1997). However, subsequent processes affecting the vapour mass can modify the original oceanic signature through the following: 1) mixing of evaporated water vapour from continental surfaces and surface water bodies (Gat et al., 1994); 2) secondary evaporation of precipitation as it falls from the cloud-base (Fritz et al., 1987); and 3) evaporation of precipitation if it sits unprotected in the rain gauge (Harvey, 2005).

2.1.2 Temporal and Spatial Variations

As precipitation is the major contributor to a given hydrologic system(s), the use of the stable isotopes ^{2}H and ^{18}O in groundwaters and surface waters in a hydrologic system(s) requires adequate spatio-temporal characterization of the stable isotopic composition of ^{2}H and ^{18}O in the local precipitation (Harvey and Welker, 2000). Temporal and spatial variations of ^{2}H and ^{18}O in precipitation are generally characterized by strong linear correlations between ^{2}H and ^{18}O, reflecting mass-dependent partitioning of $^{1}H_2{}^{16}O$, $^{1}H^{2}H^{16}O$ and $^{1}H_2{}^{18}O$ within the hydrological cycle (Gibson et al., 2005).

Temporal and spatial variations of ^{2}H and ^{18}O in precipitation are related to equilibrium and non-equilibrium (kinetic) isotopic fractionation processes that occur during the evaporation and condensation of atmospheric water vapour and its subsequent cooling (Araguas-Araguas et

al., 2000). The two main factors controlling the stable isotopic composition of precipitation at any given location are (1) the isotopic composition of the condensing parent vapour, which is largely controlled by the meteoric history of the condensing air mass, and (2) the temperature of condensation, where both temperature and physical state of the condensate determine the isotopic partitioning of ^{2}H and ^{18}O in the condensate (Araguas-Araguas et al., 2000; Ingraham, 1998). The meteoric history of the condensing air mass includes such factors as (1) meteorological conditions at the source region of the vapour mass from which the precipitation is derived (*i.e.*, relative humidity and wind speed in the atmosphere above the ocean surface, and ocean surface temperature), (2) the degree of rainout, (3) second-order kinetic effects such as snow formation or evaporation of raindrops before they reach the ground (secondary evaporation), and (4) recycling of water (mixing) along the atmospheric trajectory of the vapour mass (Clark and Fritz, 1997). Empirical relationships ("effects") were identified by Dansgaard (1964) between the isotopic composition of precipitation and environment parameters such as surface air temperature, amount of precipitation, latitude, altitude and distance to the coast. These effects are the result of the two major factors described above, and can be viewed as a measure of the mean amount of rainout of moisture that moves from the source area to the location of precipitation (Araguas-Araguas et al., 2000). The effect relating surface air temperature and the isotopic composition of precipitation is observed as a decrease of ~1 ‰ in the average annual $\delta^{18}O$ value with a corresponding decrease of ~1.1 to 1.7 °C in the average annual temperature (Dansgaard, 1964).

Assuming an isolated air mass, the partitioning of ^{2}H and ^{18}O from vapour during rainout can be described by the Rayleigh distillation process. As an air mass cools, the decrease in temperature causes it to lose its water vapour as precipitation. During rainout, the heavier

isotopes (^{2}H and ^{18}O) are preferentially partitioned into the precipitate while the residual vapour mass becomes enriched in the lighter isotopes (^{1}H and ^{16}O, respectively) and depleted in the heavier isotopes. Subsequent rains are progressively enriched in the heavier isotopes with respect to the remaining vapour, however, they are progressively depleted in the heavier isotopes with respect to earlier rains from the same vapour mass (Clark and Fritz, 1997). Within southwestern Canada, a negative (depleting) isotopic gradient exhibited by precipitation falling from Vancouver, British Columbia east towards the Continental Divide, was interpreted in terms of a single-stage Rayleigh distillation process affected by change in altitude (Yonge et al., 1989). However, the evolution of precipitation is much more complicated, as vapour masses can be affected by evaporation and recycling of rain as it falls and atmospheric mixing of vapour masses (Clark and Fritz, 1997).

2.1.3 Isotopic Composition of Groundwaters

In temperate climates, the isotopic composition of ^{2}H and ^{18}O in shallow groundwaters is generally close to the mean-weighted annual isotopic composition of local precipitation (Clark and Fritz, 1997; Froehlich et al., 2005; Gat, 1996). Gunyakti et al. (1993) in summarizing work by others, indicate that when only a portion of the annual rainfall recharges groundwater, the isotopic composition of groundwater may not be similar to the mean isotopic composition of precipitation. For ancient waters recharged in the late Quaternary, the isotopic composition of ^{2}H and ^{18}O in groundwaters may be conserved in deep aquifers (Gat, 1996). In semi-arid environments, the isotopic composition of ^{2}H and ^{18}O in shallow groundwaters can be significantly modified (*i.e.*, more positive) from that of local precipitation, as a result of evaporative isotopic enrichment during infiltration (Clark and Fritz, 1997). It should be noted, however, that Clark and Fritz (1997) and the IAEA (September 2008) provide many examples

for semi-arid regions in Central Africa where the stable isotopic composition of shallow groundwaters is similar to the mean weighted annual composition of local precipitation.

2.1.4 Isotopic Composition of Evaporative Surface Water Bodies

In semi-arid environments, the isotopic composition of ^{2}H and ^{18}O in surface waters can be modified by non-equilibrium evaporation, whereby water molecules containing the heavier isotopes - $H_2{}^{18}O$ and $^{2}H^{1}H^{16}O$ - are diffused at a lower rate than water molecules containing the lighter isotopes - $^{1}H_2{}^{16}O$ (Clark and Fritz, 1997; Gat, 1981; Gibson et al., 2005; Gonfiantini, 1986). Surface waters that have undergone evaporation are more enriched in ^{2}H and ^{18}O than the resulting water vapour (Froehlich et al., 2005). The degree of isotopic enrichment of evaporating surface waters is dependent on meteorological factors such as: atmospheric relative humidity, surface water temperature and salinity (Clark and Fritz, 1997; Gonfiantini, 1986; Rozanski et al., 2001). The isotopic composition of evaporating surface waters evolves along a line at a slope that is less than that of the global and/or local meteoric water line (*i.e.*, < 8) and that originates at the initial isotopic composition of the water prior to evaporation (Clark and Fritz, 1997; Rozanski et al., 2001). The linear trend exhibited by increasing ^{2}H and ^{18}O is commonly referred to as the local evaporation line (LEL) (Gibson et al., 2005). Evaporating water is isotopically characterized by (1) displacement of the isotopic composition of the evaporating water body below (to right-hand side of) the LMWL in the $\delta^{2}H$-$\delta^{18}O$ diagram, along the LEL; and (2) limited isotopic enrichment of the heavy isotopic water molecules (Horita et al., 2008).

In conditions where humidity is less than 100%, water-vapour exchange is minimized and non-equilibrium evaporation of surface waters occurs as evaporated water vapour leaving the system is no longer in continuous equilibrium with the water (Clark and Fritz, 1997). Gat (2008), in summarizing the work of Craig (1957), indicated that the non-equilibrium

fractionation factor for ^{18}O at normal temperatures is greater than the equilibrium fractionation factor by almost a factor of 2.

The Craig and Gordon model (1965) was developed for evaluating the isotopic composition of the evaporation flux into an open (unsaturated) atmosphere. It describes the evaporative flux relative to three regions above the water surface: (1) an interface (boundary) layer that is 100% water-saturated and in isotopic equilibrium with the underlying water column; (2) a laminar layer where transport of water vapour is dominated by molecular diffusion and non-equilibrium enrichment takes place when humidity is less than one; and (3) a turbulent section that is present at the base of the open atmosphere and where eddy diffusion and turbulent transport occur (Clark and Fritz, 1997; Horita et al., 2008). Isotopic fractionation occurs in the interface and laminar layers, however, it does not occur in the turbulent section thus giving an isotopic profile that is a mixing profile (Clark and Fritz, 1997). The total isotope fractionation (ε^*) between the water column and open atmosphere is the sum of the equilibrium fractionation factor for water-vapour exchange between the water column and the boundary layer (ε), which is based on the equation by Majoube (1971):

$$\varepsilon^{18}O_{v\text{-}l} = -(1.137(10^6/T^2) - 0.4156(10^3/T) - 2.0667) \quad (2.5)$$

for temperature T in Kelvin and the kinetic (non-equilibrium) factor for exchange between the boundary layer and laminar layer ($\Delta\varepsilon$), which is based on the equation by Gonfiantini (1986) (Clark and Fritz, 1997):

$$\Delta\varepsilon^{18}O_{v\text{-}bl} = -(14.2*[1-h])‰ \quad (2.6)$$

The equation for the enrichment of the $\delta^{18}O$ of water with respect to the $\delta^{18}O$ of vapour is:

$$\varepsilon^* = \varepsilon^{18}O_{l\text{-}v} + \Delta\varepsilon^{18}O_{bl\text{-}v} \quad (2.7)$$

This is a positive isotopic enrichment and results in a positive value. The equation for the enrichment of the $\delta^{18}O$ of vapour with respect to the $\delta^{18}O$ of water is the reciprocal:

$$\varepsilon^* = \varepsilon^{18}O_{v\text{-}l} + \Delta\varepsilon^{18}O_{v\text{-}bl} \quad (2.8)$$

This is a negative isotopic enrichment and results in a negative value.

The key parameter in the Craig and Gordon (1965) model is the isotopic composition of the evaporation moisture (δ_E). δ_E can be estimated by the following equation that was developed by Craig and Gordon (1965) and modified by Gibson (2002) to utilize isotope data in the delta per mil notation:

$$\delta_E = (\delta_L - h\delta_A - \varepsilon^*) / (1 - h + \Delta\varepsilon/1000) \quad (2.9)$$

where, δ_L is the isotopic composition of the lake water; h is the humidity normalized to the lake surface temperature; δ_A is the isotopic composition of ambient atmospheric moisture; ε^* is the total isotope fractionation between the liquid and vapour phases: $\varepsilon^* = \varepsilon + \Delta\varepsilon$ (Equation 2.8). When calculating δ_E, the isotopic composition of ambient atmospheric moisture, δ_A, can be assumed to be in equilibrium with the isotopic composition of precipitation, δ_P, and therefore, $\delta_A = \delta_P - \varepsilon$ (Gat and Bowser, 1991).

The evaporation-to-inflow ratio (E/I) can be used to determine the relative influence of evaporation and water inflow on the water balance of a water body, as in Gibson et al. (1996), Gibson (2002), Wolfe et al. (2007), Ferguson et al. (2007) and Pham et al. (2009). The E/I ratio provides the fraction of water loss by evaporation (Ferguson et al., 2007). The equation for E/I for $\delta^{18}O$ (taken from Ferguson et al., 2007) incorporates the δ_E parameter, and is expressed as:

$$E/I_{\delta 18O} = (\delta^{18}O_L - \delta^{18}O_I)(1 - h + \Delta\varepsilon^{18}O) / (\delta^{18}O_L + 1)(\Delta\varepsilon^{18}O + \varepsilon/\alpha) + h(\delta^{18}O_A - \delta^{18}O_L) \quad (2.10)$$

where, δ_I is the isotopic value of input waters into the water body, and $\varepsilon = \alpha + 1$, where α is the fractionation factor. The remaining parameters are defined above. Calculation of E/I assumes

the body of water is (1) a closed basin, receiving water only from precipitation; (2) well mixed; and (3) in isotopic steady-state (Gibson and Edwards, 2002). In view of assumption 1, δ_I can be estimated as the isotopic composition of precipitation (δ_P).

2.1.5 Age Dating

The age of a groundwater sample has most recently been defined as the average of the lengths of time that each water molecule has spent in the subsurface (Bethke and Johnson, 2008). This definition assumes that a given groundwater sample is not derived from a single molecule. Rather, groundwater is a composite of several source waters that have been affected by hydrodynamic dispersion (molecular diffusion + mechanical dispersion) and/or mixing from different source regions (Bethke and Johnson, 2008). Deep and/or regional groundwater systems can be recharged by mixtures of both modern and older water, and even a minor component of modern recharge (for example, from increased pumping) indicates that a hydraulic connection exists with an active flow regime (Bouhlassa and Aiachi, 2002). Groundwater radiometric ages are estimated from techniques that utilize: (1) known decay rates of radioactive isotopes; (2) the introduction into the atmosphere of isotopes from nuclear testing in the 1950's and 1960's; and/or (3) the record of the release of manufactured gases (Bethke and Johnson, 2008). Suitable age dating techniques are based on the age of the groundwater, where young groundwaters employ methods whose dating range encompasses the post-thermonuclear period over the last 1 to 60 years, and old groundwaters employ methods whose dating range extends from 60 to 50,000 years (Kazemi et al., 2006).

2.1.5.1 Radiocarbon Age Dating

2.1.5.1.1 ^{14}C

Carbon-14 (^{14}C) is a radioactive isotope of carbon, having six protons and eight neutrons and a half life of 5,730 years. ^{14}C refers to the ratio of ^{14}C to total stable carbon (*i.e.*, $^{14}C/^{12}C + ^{13}C$). ^{14}C is formed naturally by cosmic-ray bombardment of nitrogen in the upper atmosphere, where it rapidly oxidizes to $^{14}CO_2$, mixes into the lower atmosphere and is assimilated in the biosphere and hydrosphere (Kalin, 2000). ^{14}C is also formed artificially by thermonuclear testing (Kazemi et al., 2006). The main source of ^{14}C in groundwater is typically from CO_2 in the soil zone, as the soil zone contains up to 100 times the concentration of CO_2 than that of the atmosphere (Kalin, 2000). Radiocarbon originating from atmospheric ^{14}C is dissolved in infiltrating rainwater and from CO_2 in the soil zone (Kazemi et al., 2006) and taken into solution as dissolved inorganic carbon (DIC), thereby, giving groundwater its radiocarbon content (Bouhlassa and Aiachi, 2002). If no further ^{14}C exchange occurs under closed system conditions, ^{14}C decays to nitrogen ($^{14}C \rightarrow {}^{14}N + \beta^-$) and measurement of the remaining ^{14}C in the groundwater provides an age following the simplified decay law:

$$t = -1/\lambda_{14C} \ln(^{14}C_o/^{14}C) \quad (2.11)$$

where, t is the travel time (or, residence time) in years between the recharge location and the sampling location, λ_{14C} is the decay constant of ^{14}C of 1.21×10^{-4} year^{-1}, $^{14}C_o$ is the initial activity (at t = 0) assuming no decay occurs and ^{14}C is the measured activity of the groundwater sample (Kazemi et al., 2006).

Proper interpretation of ^{14}C measurements, and, thus, an accurate radiocarbon age, can be hindered by processes affecting the initial activity ($^{14}C_o$) of the infiltrated rainwater, including (1) input of, and subsequent dissolution of, CO_2 into soils from the decay and root respiration of

vegetation and bacterial degradation of organic matter; (2) recent contributions from natural and artificially-produced ^{14}C; and (3) modern-day fossil fuel burning, which contributes ^{14}C-free CO_2 to the atmosphere, thereby, diluting the ^{14}C concentration in the atmosphere (Kazemi et al., 2006). Upon leaving the soil zone, geochemical processes in groundwater can also modify the ^{14}C concentrations in groundwater (and, thus, the radiocarbon age), including those which contribute ^{14}C-free carbon to the groundwater, thereby, diluting the ^{14}C concentration in the groundwater and effectively "aging" the water (*i.e.*, dissolution of carbonate, sulphate reduction, oxidation of old organic matter), and those which could potentially remove ^{14}C from the groundwater (*i.e.*, precipitation of calcite, CO_2 degassing) (Kazemi et al., 2006). Various correction methods, as summarized by Kalin (2000), are available to account for these geochemical modifying processes. Molecular diffusion of ^{14}C from a confining layer into an aquifer, or from a fracture into a rock matrix, can affect the transport of ^{14}C in the subsurface, as discussed in Kazemi et al. (2006). ^{14}C concentrations of the DIC in groundwater are reported in percent modern Carbon (pmC), where the modern activity of ^{14}C is set as 13.56 decays-per-minute per gram of carbon (Kalin, 2000). The reference (or, zero) year for this activity is 1950 AD, and, thus, radiocarbon age dates go back in time from 1950 (Kalin, 2000). This reference year is considered to have an activity of 100 pmC; therefore, groundwater samples with an activity lower than 100 pmC are pre-1950 AD, and samples with an activity higher than 100 pmC are younger (Kalin, 2000).

2.1.5.1.2 $\delta^{13}C$-DIC

Large differences exist in ^{13}C among various carbon reservoirs in a regional flow system, and, thus, $\delta^{13}C$ values in groundwater can be used to evaluate geochemical reactions in the groundwater system (Hutchings and Petrich, 2002). The evolution of DIC and its associated

$\delta^{13}C$ values in groundwater begins with atmospheric CO_2 that has a $\delta^{13}C$ value of roughly -7‰ Vienna Pee-Dee Belemnite (VPDB) (Clark and Fritz, 1997). Isotopic fractionation of $\delta^{13}C$ during (C_3) plant uptake of CO_2 results in an overall depletion of 22‰, giving an average $\delta^{13}C$ value of -27‰ (Clark and Fritz, 1997). Subsequent fractionation of about 4‰ during plant decomposition results in soil CO_2 with $\delta^{13}C$ values of roughly -23‰ (Clark and Fritz, 1997). Dissolution of soil CO_2 into infiltrating water becomes hydrated and dissociates into HCO_3^- and CO_3^-, resulting in further fractionation of $\delta^{13}C$ to values of around -15‰, depending on pH (Clark and Fritz, 1997). For groundwaters in carbonate media, or media containing carbonate minerals, dissolution of carbonate results in the evolution of $\delta^{13}C$-DIC to more enriched values, depending on whether dissolution is occurring in a open or closed system with respect to CO_2 (Clark and Fritz, 1997)

2.1.5.2 ^3H and $^3H/^3He$ Age Dating

^3H is a radioactive isotope of hydrogen, having one proton and two neutrons and a half life of 12.4 years. ^3H is formed naturally by cosmic-ray bombardment of nitrogen and ^2H in the upper atmosphere and in minor amounts by neutron radiation of lithium in bedrock; and artificially by thermonuclear testing and nuclear reactor operations, as summarized in Kazemi et al. (2006) and Solomon and Cook (2002). In the atmosphere, ^3H replaces one of the hydrogen atoms in the water molecule, forming tritiated water (THO) that falls to the ground as precipitation and enters the groundwater system as recharge (Kazemi et al., 2006). As ^3H forms part of the water molecule itself, it is the only direct method available for age dating groundwater (Clark and Fritz, 1997). ^3H concentrations in groundwater are expressed in TU units, where one TU represents one THO molecule in 10^{18} water molecules (Kazemi et al., 2006). Pre-bomb (natural) ^3H levels in precipitation ranged from 0.5 to 20 TU (Kazemi et al., 2006), while ^3H

levels in precipitation in the northern hemisphere following nuclear testing in the Arctic in the early 1960's were in excess of 5,000 TU (Solomon and Cook, 2002). Concentrations of ^3H in groundwater signify atmospheric levels of ^3H when the water was last in contact with the atmosphere, and, thus, can be used to estimate the date of groundwater recharge (Motzer, 2007). If the initial concentration of ^3H (^3H_o) in the recharge water is known, then the age that the water was recharged can be calculated using the equation:

$$t = -1/\lambda_{3H} \ln(^3H_o/^3H) \quad (2.12)$$

where, t is the age of recharge and λ_{3H} is the decay constant of ^3H of 0.23 year^{-1} (Kazemi et al., 2006). Most often, the initial concentration of ^3H in the recharge water is not known, however, if water is suspected to be less than about 60 years old, a "ball-park" groundwater age can be estimated from ^3H values, where: sub-modern water (<1950's) contains <0.8 TU; a mixture of sub-modern and modern water has 0.8 to 4 TU; modern water (<5 to 10 years) contains 5 to 15 TU; water with some nuclear testing ^3H (1980's to early-mid 1990's) has 15 to 30 TU; and water with nuclear testing ^3H (1960's to 1970's) has >30 TU (Motzer, 2007).

A more accurate method to determine the age of groundwater recharge is to measure the relative abundance of ^3H and helium-3 (^3He) in a groundwater sample. ^3H decays to $^3He_{tri}$ (tritiogenic helium) and the age of groundwater recharge can be estimated using the simplified equation (Solomon and Cook, 2002):

$$t = 1/\lambda_{3H} \ln(1 + {}^3He_{tri}/^3H) \quad (2.13)$$

This equation does not require the initial concentration of ^3H (^3H_o), although, the sum of the amount of $^3He_{tri}$ from the decay of ^3H and the amount of ^3H remaining in the sample ($^3He_{tri} + {}^3H$) is equivalent to the amount of ^3H present at the time of recharge, or the initial value (Kazemi et al., 2006). The component of ^3He from the decay of ^3H must be corrected for other sources of

^{3}He such as atmospheric ^{3}He, fission of ^{6}Li by neutrons, and mantle ^{3}He (Kazemi et al., 2006). These sources each have their own distinctive $^{3}He/^{4}He$ ratios, which, in turn, result in specific $^{3}He/^{4}He$ ratios in the groundwater (Kazemi et al., 2006). In young, shallow groundwaters, the latter two sources are generally insignificant; atmospheric ^{3}He, however, must be separated from tritiogenic helium by measuring the ^{4}He content in the groundwater sample and calculating the $^{3}He/^{4}He$ ratio of the sample (Kazemi et al., 2006). This method is sensitive to excess air and does not account for travel time in the unsaturated zone (Kazemi et al., 2006).

2.2 Isotopes of NO_3

There are two stable isotopes of nitrogen: ^{15}N and ^{14}N, and three stable isotopes of oxygen: ^{16}O, ^{17}O and ^{18}O. The stable isotopes of nitrogen and oxygen are measured as the ratio of the two most abundant isotopes of a given element (for oxygen, these are ^{16}O and ^{18}O) (Clark and Fritz, 1997). The isotopic compositions of a sample are reported relative to the VSMOW reference for oxygen, and to atmospheric nitrogen (AIR) for nitrogen, and are expressed in the delta per mil (Equation 2.1), where, R_{sample} and $R_{standard}$ denote the $^{18}O/^{16}O$ or $^{15}N/^{14}N$ isotopic ratios in the sample and the reference material, respectively (Clark and Fritz, 1997).

2.2.1 Isotope Fractionation

A simplified diagram showing the N cycle in an agricultural setting is shown in Figure 2.1, modified from Davies (2000), and shows that sources of NO_3 are related to chemical processes on N in the soil zone (Kreitler, 1979). Chemical reactions such as volatilization, nitrification and denitrification can alter the isotopic ratios of N bearing compounds (Clark and Fritz, 1997). Isotope fractionation between the isotopes occurs as a function of the difference in mass of each isotope of a given element (Broecker and Oversby, 1971). Isotope fractionation is dependent on equilibrium processes (*i.e.*, NH_3 and NH_4 in solution during volatilization) and

kinetic processes (*i.e.*, reduction of NO_3 during denitrification) affecting each isotope (Clark and Fritz, 1997; Widory et al., 2004). In general, the effects of kinetic fractionation are more significant than those of equilibrium fractionation in low-temperature environments (Kendall, 1998). Each isotope fractionation process has an associated fractionation factor, defined as (for kinetic processes):

$$\alpha_{p\text{-}r} = R_p/R_r \qquad (2.14)$$

where (for isotopic fractionation of ^{15}N), $\alpha_{p\text{-}r}$ is the fractionation of the product relative to the reactant, R_p the ratio of ^{15}N to ^{14}N of the product, and R_r the ratio of ^{15}N to ^{14}N of the reactant (Kendall and Aravena, 2000). The literature reports a wide variety of fractionation factors for any particular reaction (as α, β and ε values) and values are defined in different ways by different authors (Kendall, 1998). Kendall (1998) strongly advises that fractionation factors established in one study cannot be directly applied to other studies, as the amount of fractionation is highly dependent on the local environment. Where isotope fractionations are

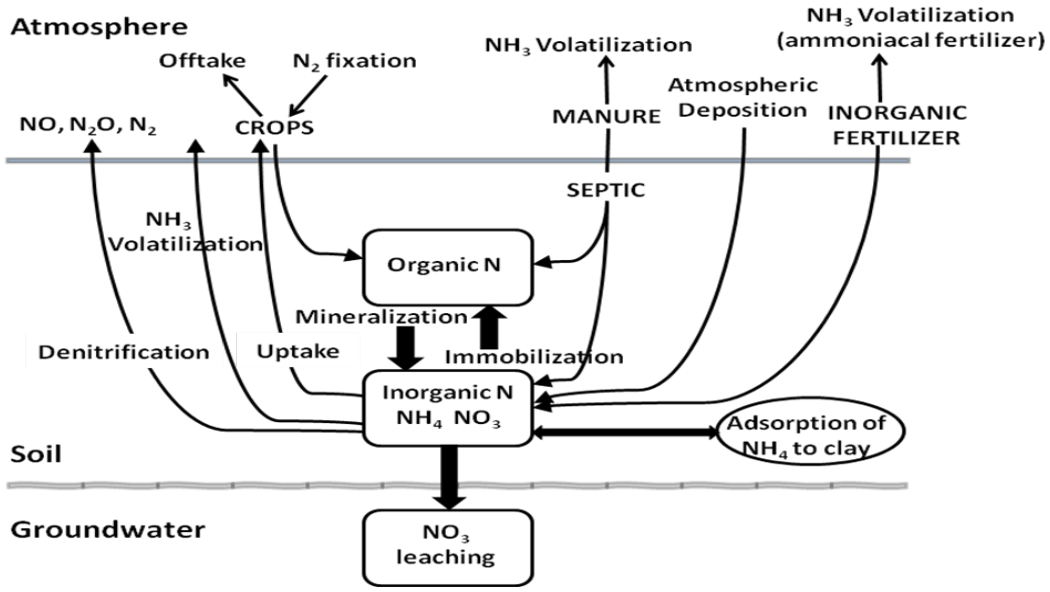

Figure 2.1. Simplified N cycle in an agricultural setting (modified from Davies, 2000).

small, an enrichment factor, ε, can be used to approximate the isotopic difference of R_p/R_r in per mil (‰) notation (Clark and Fritz, 1997):

$$\varepsilon_{p\text{-}r} = (R_p/R_r - 1)\cdot 10^3 = (\alpha - 1)\cdot 10^3 \quad (2.15)$$

As a general rule, most of the isotope fractionation is caused by the slowest, or 'rate-determining', step (Kendall, 1998). A 'rate-determining' step typically involves a large reservoir of reactant where the amount of material actually used is smaller than the size of the reservoir (Kendall, 1998). A step that is not 'rate-determining' typically involves a small reservoir of material that is instantly converted from reactant to product, resulting in no isotope fractionation at that step (Kendall, 1998).

2.2.2 N- and O-Transforming Processes

N and O dynamics in soil and groundwater are controlled by biologically-mediated reactions (*i.e.*, assimilation, nitrification and denitrification) and physical processes (mainly, volatilization), where each reaction, and each step of the reaction, has the potential for isotope fractionation (Kendall and Aravena, 2000). The overall isotope fractionation depends on local environmental conditions, including the number and type of intermediate steps, the size of reservoirs of the various compounds involved in the reactions, soil pH, and species of the organism (Kendall, 1998). Because of the complexities associated with N isotope fractionations, the determination of NO_3 sources by means of stable isotopes is more qualitative than quantitative (Spalding et al., 2001). Reactions controlling N dynamics in an agricultural setting are discussed in detail below.

2.2.2.1 Mineralization

Mineralization, or ammonification, refers to microbial conversion of organic N (*i.e.*, proteins, chitins, amino sugars from microbial cells, and nucleic acids) to inorganic N as

ammonium (NH_4) (Pierzynski et al., 2005). Mineralization is the first step of the simplified progression (Kendall and Aravena, 2000):

$$\text{Organic-N} \rightarrow NH_4 \rightarrow NO_2 \rightarrow NO_3 \quad (2.16)$$

As most (>95%) of the reduced N in soils is in the organic form (Pierzynski et al., 2005), microbial conversion of organic N to NH_4 is a necessary process for growth of terrestrial plants that do not fix atmospheric nitrogen (N_2), but rather obtain N from soil NH_4 or NO_3 to synthesize organic N (Clark and Fritz, 1997; Dinnes et al., 2002). Organic N may be naturally present in the soil, it may be added as animal manures and municipal by-products, or it may be released during the decay of biomass (crop residue) (Pierzynski et al., 2005). Note, that in nutrient poor soils, application of inorganic fertilizer N provides a readily available source of N to the plant as NH_4 or NO_3 (Dinnes et al., 2002). During mineralization, ^{14}N is preferentially incorporated into plants over ^{15}N (Clark and Fritz, 1997). However, only small isotope fractionation occurs, thus, only slightly altering the ^{15}N of the residual fertilizer or soil organic matter (Kendall, 1998). In general, ^{15}N of soil NH_4 is usually within ±1‰ of the composition of total organic N in the soil (Kendall, 1998). Crop plowing or tillage stimulates mineralization of soil organic N, by aerating the soil zone and increasing the availability of oxygen to soil microbes (Dinnes et al., 2002; Kreitler et al., 1978; Mengis et al., 2001). Mineralization rates are usually impeded by winter temperatures, however, as soils warm in the spring, mineralization rates increase, more or less coinciding with N uptake and plant growth (Powlson, 1993). Mineralization can continue long after plants have ceased taking up N, thus, resulting in available N for nitrification and accumulation of NO_3 during the late summer through to the early winter (Powlson, 1993).

Mengis et al. (2001) provide a discussion on “mineralization-immobilization turnover”, where NO_3 from inorganic fertilizers is rapidly immobilized as organic N by incorporation into

the microbial biomass, releasing the three oxygen atoms in the process. Immobilized organic N is subsequently re-mineralized to NH_4 and then oxidized back to NO_3 under aerobic conditions (Mengis et al., 2001). This process is inferred to significantly modify $^{18}O_{NO3}$ and $^{15}N_{NO3}$ of inorganic NO_3 fertilizers (Mayer et al., 2001; Mengis et al., 2001), however, it would be negligible when NO_3 is rapidly transported through the soils (*i.e.*, as a result of irrigation) (Mengis et al., 2001).

2.2.2.2 Nitrification

Nitrification is a multi-step oxidation process that is mediated by autotrophic organisms in order to derive metabolic energy" (Kendall, 1998). Nitrification refers to the oxidation of NH_4 from fertilizers, septic waste and manures, and/or mineralized soil organic N by *Nitrosomonas* bacteria to NO_2, followed by the oxidation of NO_2 by *Nitrobacter* bacteria to NO_3, as shown by the following overall reaction (Freeze and Cherry, 1979; Kendall, 1998)

$$NH_4 + 2O_2 \rightarrow NO_3 + + 2H^+ + H_2O \quad (2.17)$$

Nitrite (NO_2), NO or N_2O can also be end products of nitrification. Along with NO_3, nitrification generates acidity as microbial oxidation of NH_4 releases protons (H^+) (Freeze and Cherry, 1979). NO_3 produced by nitrification derives two oxygen from oxygen in water molecules and one oxygen from dissolved O_2 (Anderson and Hooper, 1983; Aravena et al., 1993). During nitrification, N isotope fractionations depend on whether the rate-determining step is one of the nitrification reactions or non-fractionating mineralization (Bedard-Haughn et al., 2003; Kendall, 1998). The oxidation of NO_2 to NO_3 generally proceeds rapidly in natural systems, and, thus, most of the N isotope fractionation is likely a result of the slow oxidation of NH_4 to NO_2 (Bedard-Haughn et al., 2003; Kendall, 1998). The extent of isotope fractionation is generally dependent on the size of the N reservoir. In N-limited systems, isotope fractionations

are minimal and the $^{15}N_{NO3}$ of soil NO_3 is usually within a few ‰ of the composition of total organic N in the soil (Kendall, 1998). In large N reservoirs (*i.e.*, after fertilizer and/or manure application) where a large amount of NH_4 is available, nitrification can proceed with significant N isotope fractionation accumulating ^{14}N preferentially in the produced NO_3 (Mariotti et al., 1981). Here, nitrification is stimulated, and oxidation of NH_4 is the rate-determining step (Kendall and Aravena, 2000). Kendall (1998) indicates that $^{15}N_{NO3}$ of the first-formed NO_3 is low, however, as the NH_4 pool is used up, the nitrification rate decreases, the rate-determining step is no longer the oxidation of NH_4 , a decrease in the overall nitrification fractionation is observed, and $^{15}N_{NO3}$ of the total NO_3 rises towards pre-fertilization values (Figure 2.2). NO_3 in aerobic groundwaters generally have $\delta^{15}N_{NO3}$ values similar to those of the N source (Wassenaar, 1995). Nitrification rates decrease with a decrease in temperature (Sabey et al., 1956).

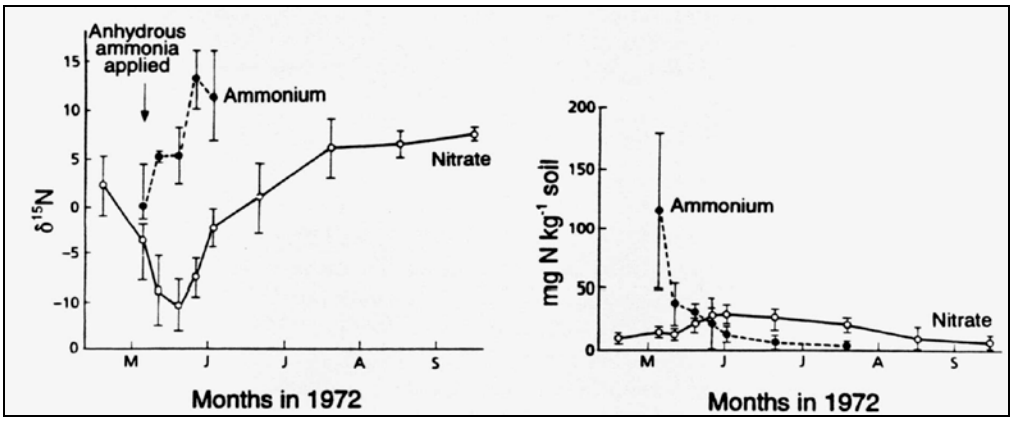

Figure 2.2. Progression of soil $\delta^{15}N_{NO3}$ values resulting from application of NH_4 fertilizer, volatilization of NH_4, and nitrification of NH_4 (from Kendall, 1998).

2.2.2.3 Volatilization

Volatilization refers to the volatile loss of ^{15}N-depleted gaseous ammonia (NH_3) from NH_4 in manure or mineral fertilizers containing urea and/or NH_4 compounds (Deutsch et al., 2006; Kendall, 1998; Kreitler, 1979). The remaining ^{15}N-enriched NH_4 is converted to ^{15}N-enriched NO_3 during nitrification (Heaton, 1986; Mayer, 2005). Both equilibrium and kinetic

fractionations occur during volatilization, and the resulting isotopic enrichments are large (Kendall, 1998). Volatilization is accelerated when alkaline soils, low soil organic matter & clay content (*i.e.*, low cation exchange capacity [CEC]), low moisture and high temperatures are present (Liu et al., 2007; Mavi and Singh, 2007; Musa, 1968; Singh et al., 1984). Application of fertilizer urea ($CO(NH_2)_2$) to soil surfaces is susceptible to volatilization. Under favourable conditions, urea is hydrolyzed by urease to NH_4 and then to NH_3 (Havlin et al., 1999; Henry et al., 1999), as shown by:

$$CO(NH_2)_2 + H^+ + 2H_2O \rightarrow 2NH_4 + HCO_3 \quad (2.18)$$

$$NH_4 \rightarrow NH_{3(aqueous)} + H^+ \text{ (in soil solution)}$$

$$NH_{3(aqueous)} \rightarrow NH_{3(atm)} \text{ (from soil solution to atmosphere)}$$

Equation 2.18 shows that hydrolysis of urea generates alkalinity during conversion to NH_4, and volatilization generates acidity during NH_4 conversion to NH_3. Urea hydrolysis proceeds rapidly, with most of the urea transformed to NH_4 in several days (Mavi and Singh, 2007; Musa, 1968).

2.2.2.4 Denitrification

Denitrification is a multi-step process involving a biologically mediated reduction of NO_3 to N_2, where nitrogen oxides (N_2O, NO) are intermediate compounds (Kendall, 1998). Denitrification requires the presence of denitrifying bacteria, reducing conditions (*i.e.*, very low oxygen levels), and an electron donor (Delwiche, 1981). Denitrification occurs when denitrifying bacteria obtain energy by catalyzing a redox reaction in which an electron donor is oxidized while NO_3 is reduced (Rodvang and Simpkins, 2001). Microbial denitrification primarily occurs during NO_3 reduction by heterotrophic *Pseudomonas denitrificans* and simultaneous respiration of CO_2 from oxidation of organic matter (Kendall, 1998):

$$4NO_3 + 5C + 2H_2O \rightarrow 2N_2 + 4HCO_3 + CO_2 \quad (2.19)$$

Microbial denitrification can also occur during autotrophic respiration of *Thiobacillus denitrificans*, where reduced sulphur or reduced iron are used as electron donors (Kendall and Aravena, 2000). Denitrification causes $^{15}N_{NO3}$ and $^{18}O_{NO3}$ of residual NO_3 to increase exponentially as NO_3 concentrations decrease (Kendall, 1998), resulting in a ~ 2:1 enrichment in $^{15}N_{NO3}$ and $^{18}O_{NO3}$, respectively (Amberger and Schmidt, 1987). As shown by equation 2.19, denitrification causes the acidity of the system to decrease. Whereas NH_4 is readily exchangeable and can be adsorbed to soil and aquifer matrices, NO_3 may move unimpeded unless denitrification occurs (Behnke, 1975; Karr et al., 2001).

2.3 Sources of NO_3

2.3.1 $\delta^{15}N_{NO3}$

2.3.1.1 Synthetic Fertilizer

Synthetic fertilizers, including urea, ammonium-nitrate (NH_4-NO_3) and potassium nitrate, are produced by the fixation of atmospheric N and have $\delta^{15}N$ values ranging from -4 to +4‰, reflecting the ^{15}N isotopic composition of their atmospheric source (*i.e.*, 0‰) (Flipse and Bonner, 1985; Kendall and Aravena, 2000; Wassenaar, 1995). As urea is both safe and cost-effective, its increased production and consequent worldwide use as a fertilizer source has contributed to its increase of more than 100-fold in the last four decades, with a doubling in the past decade (Glibert et al., 2006).

2.3.1.2 Septic Waste and Manure

Where subsurface conditions are aerobic, NO_3 can form from the nitrification of NH_4 present in septic waste (Aravena et al., 1993). Septic waste generally has $\delta^{15}N$ values in the range of +10 to +25‰ (Heaton, 1986; Kendall, 1998). The range in $\delta^{15}N_{NO3}$ values of manure is

similar to those of septic waste, from approximately +10 to +25‰ (Heaton, 1986; Karr et al., 2001; Kendall, 1998; Wassenaar, 1995). NO_3 derived from manure generally takes on an isotopic signature that is enriched in ^{15}N due to volatilization of gaseous NH_3 during storage and application (Kendall, 1998).

2.3.1.3 Soil Nitrogen

Organic N, present in soils as a result of plant decomposition and microbial activity, can be oxidized in the subsurface to form NO_3 (Kendall and Aravena, 2000). $\delta^{15}N_{NO3}$ values derived from soil organic N range from approximately +4 to +9‰ (Heaton, 1986), with the average in the range of +2 to +5‰ (Kendall, 1998). NO_3 derived from organic N, and not by anthropogenic N sources, is generally present in groundwater at concentrations below 9 mg/l (~2 mg/l as N) (Edmunds and Gaye, 1997). When concentrations of NO_3 in groundwater are consistently lower than 3 mg/l as N, and corresponding $\delta^{15}N_{NO3}$ values range from +5 to +8‰, then naturally occurring soil N can be assumed to be the source of NO_3 (Choi et al., 2003).

2.3.2 $\delta^{18}O_{NO3}$

NO_3 originating from synthetic NO_3 fertilizers produced from atmospheric O_2 has $\delta^{18}O$ values in the range of +18 to +22‰ (Amberger and Schmidt, 1987). All three oxygens in the NO_3 are derived from atmospheric O_2, which has a $\delta^{18}O$ value of +23.5‰, and, thus, $\delta^{18}O$ values in synthetic fertilizer NO_3 are similar to atmospheric O_2.

When $\delta^{18}O$ values in NO_3 are less than that of atmospheric O_2, NO_3 is being produced locally by nitrification and does not originate in synthetic NO_3 fertilizers (Seiler, 2005). Nitrification of fertilizer NH_4, soil organic N or animal/human wastes produces NO_3 with two oxygen derived from oxygen in water molecules and one oxygen derived from dissolved oxygen in the unsaturated and saturated soil zones (Anderson and Hooper, 1983; Aravena et al., 1993).

Isotope fractionation of ^{18}O is not significant during nitrification (Clark and Fritz, 1997), and, thus, if $\delta^{18}O$ values of the water and the dissolved O_2 are known (where $\delta^{18}O$ of soil $O_2 \approx \delta^{18}O$ of atmospheric air), then the $\delta^{18}O$ of the NO_3 can be calculated (Kendall and Aravena, 2000):

$$\delta^{18}O\ (_{\text{nitrate}}) = \tfrac{2}{3}\ \delta^{18}O\ (_{\text{water}}) + \tfrac{1}{3}\ \delta^{18}O\ (_{\text{dissolved O2}}) \qquad (2.20)$$

$\delta^{18}O_{NO3}$ derived by nitrification is generally in the range of -10 to +10‰ (Kendall and Aravena, 2000).

NO_3 originating from NH_4-NO_3 fertilizers, which derive 50% of their oxygen from nitrification of fertilizer NH_4^+ and the remaining 50% of their oxygen from synthetic NO_3 fertilizer, have $\delta^{18}O$ values of approximately +13 ‰ (Aravena et al., 1993). This $\delta^{18}O$ value is approximately half that of atmospheric O_2 and, thus, half that of synthetic NO_3 fertilizers.

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CHAPTER 3
STABLE ISOTOPES OF HYDROGEN AND OXYGEN IN PRECIPITATION IN THE OKANAGAN BASIN, BRITISH COLUMBIA, CANADA

Abstract. Spatio-temporal characterization of the isotope composition of ^{2}H and ^{18}O in regional precipitation is an essential component of regional groundwater and/or surface water studies that utilize stable isotopes as tracers of water. In the Okanagan Basin of British Columbia, Canada, research involving the stable isotopes of hydrogen and oxygen in precipitation, groundwater and/or surface water is currently limited. This study established a record of stable isotope compositions of ^{2}H and ^{18}O in precipitation in the Okanagan Basin, constructed local meteoric water lines based on these data, and interpreted these data in light of known meteorological and hydrological processes affecting the isotope compositions of precipitation. The climate of the Okanagan Basin is semi-arid and precipitation generally stems from Maritime Polar air masses in the winter and local convective systems in the summer. For this study, 45 precipitation samples were collected on a monthly basis from April 2006 to April 2008 at three collection stations: Osoyoos West, Osoyoos East and West Kelowna. The results showed that $\delta^{2}H$ values ranged from -177 to -66‰ and $\delta^{18}O$ values ranged from -23.0 to -6.1‰. Minimum $\delta^{2}H$ and $\delta^{18}O$ values occurred in the winter and maximum values occurred in the summer, indicative of seasonality. Using $\delta^{2}H$ and $\delta^{18}O$ values, the local meteoric water line for Osoyoos (West and East) was $\delta^{2}H=6.06\delta^{18}O–31.21$ and the local meteoric water line for West Kelowna was $\delta^{2}H=7.03\delta^{18}O–12.68$. Using amount-weighted (approximate) monthly $\delta^{2}H$ and $\delta^{18}O$ values, the local meteoric water line for Osoyoos (West and East) was $\delta^{2}H=6.00\delta^{18}O–32.04$ and the local meteoric water line for West Kelowna was $\delta^{2}H=7.18\delta^{18}O–10.69$. Summer precipitation was generally affected by secondary processes such as recycling (mixing) of water vapour and secondary evaporation, and by seasonal variation in the origin of precipitation.

Key Words: precipitation, isotopes, local meteoric water line, semi-arid, Rayleigh fractionation, secondary evaporation.

3.1 Introduction

Temporal and spatial variations of the stable isotopes of hydrogen (^{2}H) and oxygen (^{18}O) in precipitation are related to equilibrium and non-equilibrium (kinetic) isotopic fractionation processes that occur during the evaporation and condensation of atmospheric water vapour and its subsequent cooling (Araguas-Araguas et al., 2000). Temporal and spatial variations of ^{2}H and ^{18}O in precipitation are characterized by strong linear correlations between ^{2}H and ^{18}O, reflecting mass-dependent partitioning of $^{1}H_{2}{}^{16}O$, $^{1}H^{2}H^{16}O$ and $^{1}H_{2}{}^{18}O$ within the hydrological cycle (Gibson et al., 2005). The correlations between ^{2}H and ^{18}O in precipitation are a result of climatic and geographic factors, globally described as the global meteoric water line (GMWL), and regionally, as the local meteoric water line (LMWL) (Clark and Fritz, 1997).

Where modern precipitation is the major recharge source of a given hydrologic system(s), a long-term record of the stable isotopes of ^{2}H and ^{18}O can provide fundamental information for regional climatological and hydrological studies (Gat, 1996; Rozanski et al., 1993; Yurtsever, 1975). For example, ^{2}H and ^{18}O in precipitation have been used to construct local meteoric water lines (Benjamin et al., 2005; Harvey and Welker, 2000; Peng et al., 2004), to determine sources of groundwater recharge (Clark et al., 1998; Larson et al., 2000; Palmer et al., 2007; Tsujimura et al., 2007), to evaluate surface water-groundwater interactions (Gammons et al., 2006; Harvey et al., 2006), to investigate geochemical and hydrologic problems (Hazen et al., 2002; Jun et al., 2005; Koh et al., 2005) and to assess weather patterns that influence a particular region (Moran et al., 2007).

Considerable attention is currently focused on the Okanagan Basin, British Columbia, where because of increasing population growth, intensive agricultural activities, and the semi-arid climate of the region, concerns over the sustainability of the water supply, surface water-

groundwater interactions, water quality and climate change are being raised (Cohen et al., 2006; Merritt et al., 2006; Neilsen et al., 2001; Neilson-Welch and Allen, 2007). As was the case in the literature cited above, stable isotopes of precipitation provide a means of defining the hydrologic and climatological control on water resources in the Okanagan Basin. Unfortunately, the relationship between the stable isotopic composition of ^{2}H and ^{18}O in the local precipitation (*i.e.*, LMWL) for the Okanagan Basin has not yet been defined. Only three LMWLs exist in southwestern Canada: Victoria, British Columbia (Fritz et al., 1987), Calgary, Alberta (Peng et al., 2004) and Saturna Island, British Columbia (Canadian Network of Isotopes in Precipitation [CNIP], February 2008). The Canadian Meteoric Water Line (CMWL), which is based on precipitation collected at several meteorological stations throughout Canada, has also been described (Fritz et al., 1987). CNIP provides preliminary maps of average distributions of ^{2}H and ^{18}O in mean annual precipitation in Canada (CNIP, February 2008).

The objectives of this chapter were to (1) establish a record of stable isotope compositions of ^{2}H and ^{18}O in precipitation in the Okanagan Basin, (2) based on the precipitation data collected, construct preliminary LMWLs for the Basin, and (3) interpret these data in light of meteorological and hydrological processes affecting the stable isotope compositions of ^{2}H and ^{18}O in precipitation in the Okanagan Basin and the limited precipitation data from western Canada.

3.2 Study Area

3.2.1 Location

The Okanagan Basin is located in the Southern Interior Plateau of British Columbia and northern Washington (in the United States). The Basin lies in a south trending valley and includes all lands surrounding streams and lakes that discharge into the Okanagan River

(Figure 3.1). Within Canada, the Okanagan Basin extends for roughly 160km, from Armstrong (just north of Vernon) in the north to the Canada-United States border (near Osoyoos) in the south, and covers an area of approximately 8,200 km^2. The Basin extends for roughly 115km south into the United States, however, this study is focused only on the portion in Canada.

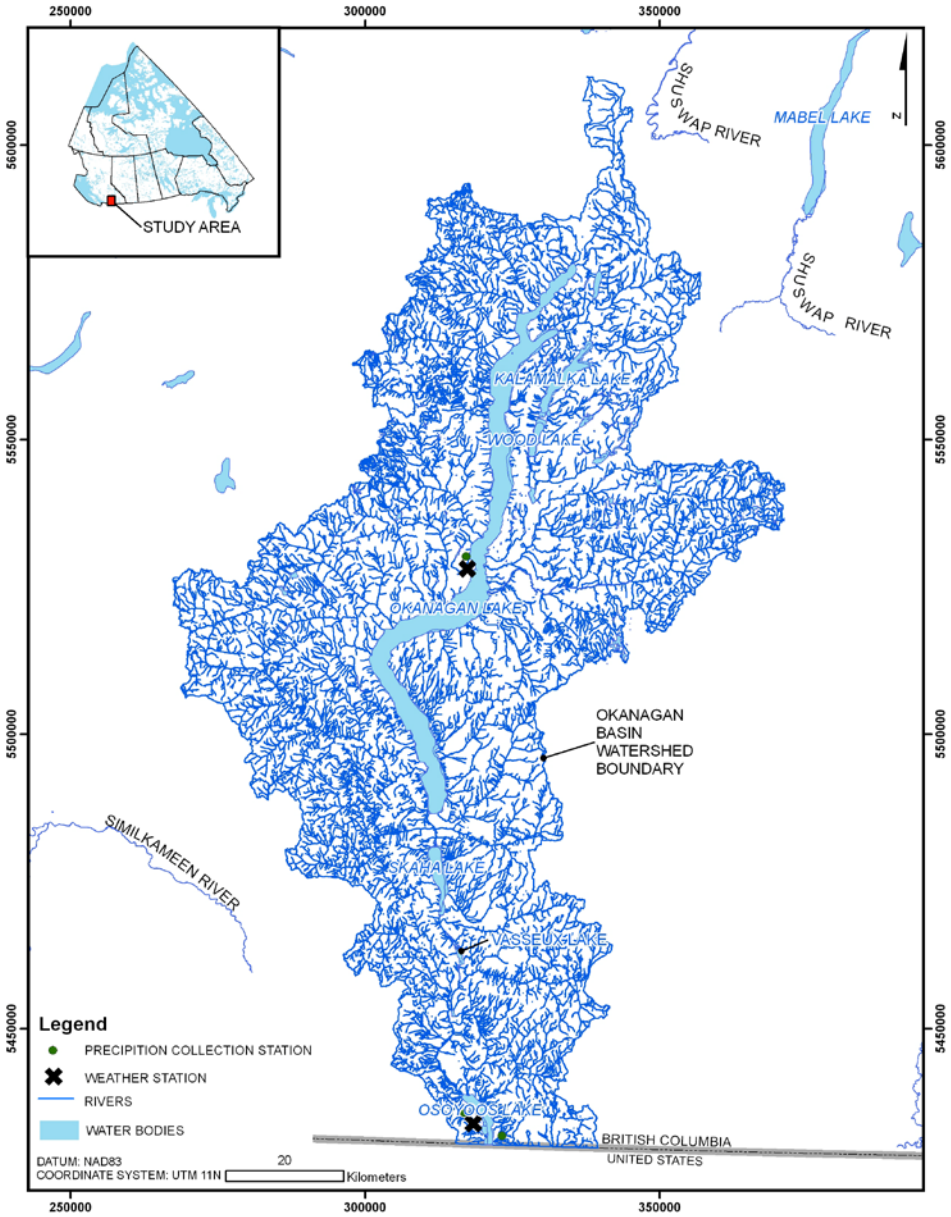

Figure 3.1. Map showing location of the Okanagan Basin, British Columbia, Canada, and approximate locations of precipitation collectors and nearby weather stations used in this study. Map produced using river data from the website www.geobase.ca (National Hydro Network, station 08nm001) and national boundary line and water body data from DMTI Spatial Inc.

3.2.2 Weather Patterns

The Okanagan Basin is located in the rain shadow of the Coast and Cascade Mountains to the west. In the winter, moist air from the Pacific Ocean (Maritime Polar air mass) is successively forced up the Coast and Cascade Mountains by prevailing westerly winds. The air mass cools and its moisture falls on the windward side of the mountains. As the air mass is then forced down the leeward side of the mountains into the Interior Plateau, it warms and dries. By the time a Maritime Polar air mass reaches the Interior, much of its moisture has been lost (BC Ministry of Environment [BC MOE], February 2008). As the larger surface water bodies (including Okanagan Lake) do not freeze over during the winter, cold air pools in the valley and inversions commonly develop, trapping moisture and supporting the development of low cloud (Klock and Mullock, 2001). The mountain ranges east of the Interior Plateau act as a barrier to the westward passage of cold Continental Arctic air masses, although, on occasion, cold air (with no moisture) from a Continental Arctic air mass does make its way over the Interior Plateau. In the summer, a Pacific high pressure system moves northward and diminishes the frequency and intensity of Pacific storms and coastal precipitation. By June, high rates of insolation and late spring surges of cool unstable air produce strengthened convective activity, resulting in showers and thundershowers (BC MOE, February 2008). In general, weather systems from the west (migrating Pacific storms) provide the majority of precipitation in winter while convective systems provide the precipitation in summer (Klock and Mullock, 2001; Merritt and Alila, 2004).

3.2.3 Climate

In general, the climate of the Okanagan Basin is dry, and classified as semi-arid. Precipitation amounts within the Basin decrease from north to south, with an average annual total precipitation of 447 mm falling in Vernon, 320 mm in Kelowna and 320 mm in Osoyoos

(Environment Canada [EC], February 2008) (Table 3.1). The greatest amount of precipitation in the Okanagan Basin generally falls in the spring (May to July). Temperatures are approximately 2 to 3 degrees cooler in the north end of the Basin than in the south (EC, February 2008) (Table 3.1). Evapotranspiration (ET), a combined measurement of water evaporated from the soil surface and transpired through the plant, is greatest in the south end of the Basin (Farmwest, July 2008). ETo rates, which are based on a grass-reference crop, reach an average of 6.6 mm/day at the south end of the Basin at Osoyoos (Agriculture and Agri-Food Canada [AAFC], December 2008), and an average of 5.7 mm/day at the north end of the Basin at Vernon (Farmwest, July 2008) (Table 3.1). The average annual water deficit in the Basin based on the difference between total precipitation and total ETp ranges from roughly 300 mm/year in Vernon to 500 mm/year in Osoyoos (AAFC, December 2008; EC, February 2008; Farmwest, July 2008). ETp, evapotranspiration measured from a pan, was calculated by multiplying ETo values by a factor of 0.8 (BC Ministry of Agriculture Food and Fisheries 2001).

Table 3.1. Summary of mean annual precipitation, mean annual temperature, and mean minimum and maximum ETo rates for Vernon, Kelowna and Osoyoos, British Columbia, Canada, for the period between 2006 and 2007.

Station	Location	Elevation (metres above sea level; masl)	Mean annual precipitation (mm)	Mean annual temp. (°C)	Mean min. ETo in December (mm/day)	Mean max. ETo in July (mm/day)
Vernon	50.34°N, 119.27°W	512	447 (2006)	9.4 (2006)	0.5	5.7
Kelowna	49.96°N, 119.38°W	430	320	7.9	0.6	6.0
Osoyoos	49.03°N, 119.44°W	297	320	11.1	0.6	6.6

3.3 Materials and Methods

Precipitation samples were collected on a monthly basis from April 2006 to April 2008 at three collection stations along the Okanagan Basin (Figure 3.1): Osoyoos West, Osoyoos East and West Kelowna. Nineteen samples were collected from the Osoyoos West collect station, situated at the Desert Centre in rural Osoyoos, 7 samples were collected from the Osoyoos East station, located at a private residence on Anarchist Mountain, and 19 samples were collected

from the West Kelowna station, located at a private residence in the District of West Kelowna. The station locations covered the range in latitude of the central and south portions of the Basin, as well as the range in elevation (from 810 masl at Osoyoos East, 580 masl at West Kelowna and 360 masl at Osoyoos West). Rainwater samples were collected in rain gauges, to which were added several mls of paraffin oil to prevent evaporation of the rainwater. Snowfall samples from Osoyoos West and West Kelowna (only) were collected in plastic containers and the snow was allowed to melt indoors prior to obtaining the sample. For several months of the year (*i.e.*, during the summer) there was insufficient to no precipitation in the collectors.

Precipitation samples were analyzed for δ^2H and $\delta^{18}O$ (n = 45 samples) at Environment Canada's National Hydrology Research Center (NHRC) in Saskatoon, SK. Sample analysis was conducted on isotope ratio mass spectrometers (IRMS) between April 2006 and April 2007 and by laser spectroscopy (Lis et al., 2008) between April 2007 and April 2008. Where IRMS was used, δ^2H values were measured by converting the water sample into H_2 gas using the standard Zn reduction technique (Coleman et al., 1982) and $\delta^{18}O$ values were measured using the standard CO_2-water equilibration technique (Epstein and Mayeda, 1953). Results were reported relative to VSMOW in the δ(‰) notation (Equation 2.1). The error in the reported values was ±2.0‰ (IRMS) or ±1.0‰ (laser spectroscopy) for δ^2H and ±0.2‰ for $\delta^{18}O$. Sample results represent the isotopic composition of combined precipitation events within an (approximate) monthly sampling interval ending on the collection date. Collection of samples from individual precipitation events was beyond the scope of this study. Four precipitation samples from Osoyoos West (October 2006, March 2007, June 2007 and November 2007) exhibited significantly lower (more depleted) δ^2H, $\delta^{18}O$ and/or d-excess values than all other samples collected during this study. The low values were likely due to evaporation during sample

storage. The δ^2H and $\delta^{18}O$ values of these four precipitation samples were compared to δ^2H and $\delta^{18}O$ values in precipitation collected approximately 15 km north of Osoyoos West in Oliver, BC, in 2008 (Hendry, 2008). Specifically, the three Osoyoos samples having δ^2H values of -55 to -68‰ were compared to three Oliver precipitation samples having δ^2H values of -53 to -65‰. The corresponding $\delta^{18}O$ values for the Osoyoos samples were approximately 2.3 to 5.3‰ more enriched than the corresponding $\delta^{18}O$ values for the Oliver samples. Additionally, none of the Oliver precipitation samples exhibited δ^2H values as enriched as the δ^2H value in the Osoyoos precipitation sample collected in June 2007 (i.e., -28‰). As a conservative measure, the δ^2H and $\delta^{18}O$ values of the four precipitation samples from this study were discarded and not discussed further.

Amount-weighted δ^2H and $\delta^{18}O$ values were estimated for all three stations using precipitation amounts recorded from nearby Environment Canada weather stations. Amount-weighted values were calculated by summing the products of the monthly precipitation amounts and monthly isotopic compositions, and dividing the sum by the total precipitation (Peng et al., 2004). Amount-weighting was used to reduce the bias imparted on the LMWL by small precipitation events. For Osoyoos West and Osoyoos East, the nearest weather station maintaining the most complete climate data set was "*Osoyoos West*" (Climate ID 1125865; 49.03ºN, -119.44ºW, 297masl) (Figure 3.1). "*Osoyoos West*" was approximately 60m lower in elevation and 5km from the Osoyoos West precipitation collector, and approximately 510m lower in elevation and 4km from the Osoyoos East precipitation collector. For West Kelowna, the nearest weather station was located at "*Quails Gate*" (Climate ID 1123993; 49.84ºN, -119.57ºW, 417masl), approximately 160m lower in elevation and 5km from the West Kelowna precipitation collector (Figure 3.1).

For precipitation samples collected concurrently from the south Okanagan Basin (West Osoyoos) and the central Okanagan Basin (West Kelowna), the δ^2H and $\delta^{18}O$ values were compared to assess any potential spatial trends in the isotopic composition of precipitation. Specifically, the data were evaluated to determine if the isotopic composition of precipitation differed from one station to the other, and to identify whether key isotopic fractionation processes (*i.e.*, secondary evaporation, rainout) were specific to one location.

Linear regression was completed for individual and amount-weighted δ^2H and $\delta^{18}O$ values for each station to define the linear regression equation (LMWL) for that station. For individual δ^2H and $\delta^{18}O$ values, statistical analysis was completed using GraphPad Prism version 5.00 for Windows, GraphPad Software, San Diego California USA to determine if the slope and intercept of the linear regression equations for each station were significantly different. The slopes and intercepts of the Osoyoos West and Osoyoos East linear regression equations were not significantly different ($P>0.05$), and therefore were pooled to form a single LMWL for "Osoyoos". The slope of the West Kelowna linear regression equation was significantly different to that of the Osoyoos linear regression equation ($P<0.05$) and subsequently the difference in the intercepts could not be tested using the GraphPad software. An independent LMWL was therefore generated for West Kelowna. The corresponding correlation coefficient (R^2) and the 95th percentile confidence interval of the Osoyoos and West Kelowna regression lines were calculated (University of Ottawa, February 2008).

A 1-way ANOVA (Kruskal-Wallis) nonparametric test, used as data were not sampled from populations that followed a Gaussian distribution, was completed for the d-excess values using the GraphPad software. The median d-excess value of precipitation samples collected at all three stations locations were not significantly different ($P<0.05$).

3.4 Results and Discussion

3.4.1 δ^2H and $\delta^{18}O$ Values

The δ^2H and $\delta^{18}O$ values of precipitation samples collected in the Okanagan Basin between April 2006 and April 2008 are presented in Table A-1 of Appendix A. The δ^2H and $\delta^{18}O$ values of precipitation samples ranged from -150 to -75‰ (average of -112 ± 25‰) and -19.0 to -6.1‰ (average of -13.4 ± 4.1‰), respectively, at Osoyoos West; -157 to -82‰ (average of -104 ± 27‰) and -18.3 to -7.5‰ (average of -11.9 ± 3.6‰), respectively, at Osoyoos East; and -177 to -66‰ (average of -108 ± 29‰) and -23.0 to -7.8‰ (average of -13.6 ± 4.0‰), respectively, at West Kelowna.

The data exhibited a clear seasonality (temperature) effect, with more depleted values occurring in the winter (November to April) and more enriched values occurring in the summer/early fall (May to October) (Figure 3.2). The average winter δ^2H and $\delta^{18}O$ values of all precipitation samples collected in the Okanagan Basin were -129 and -16.1‰, respectively. These values were comparable to δ^2H and $\delta^{18}O$ values obtained by Yonge et al. (1989) for the Southern Interior (near Penticton) in December 1986: -124 to -128‰ for δ^2H and -16.7 to -17.2‰ for $\delta^{18}O$. The average summer δ^2H and $\delta^{18}O$ values of all precipitation samples collected in the Okanagan Basin were -92 and -10.8‰, respectively. These values were more enriched than those obtained by Yonge et al. (1989).

3.4.1.1 Amount-weighted δ^2H and $\delta^{18}O$ Values

Amount-weighted annual δ^2H and $\delta^{18}O$ values of precipitation samples collected in the Okanagan Basin between April 2006 and April 2008 are presented in Table A-2 of Appendix A. The amount-weighted annual δ^2H and $\delta^{18}O$ values were -109 and -13.5‰, respectively, at Osoyoos West; -102 and -11.4‰, respectively, at Osoyoos East; and -107 and -13.5‰,

respectively, at West Kelowna. The amount-weighted annual δ^2H and $\delta^{18}O$ values of precipitation collected in the Okanagan Basin were more depleted than amount-weighted annual δ^2H and $\delta^{18}O$ values of precipitation in Victoria (-77 and -10.2‰, respectively), and more enriched than amount-weighted annual δ^2H and $\delta^{18}O$ values of precipitation in Calgary (-136 and -17.9‰, respectively) (Table 3.2).

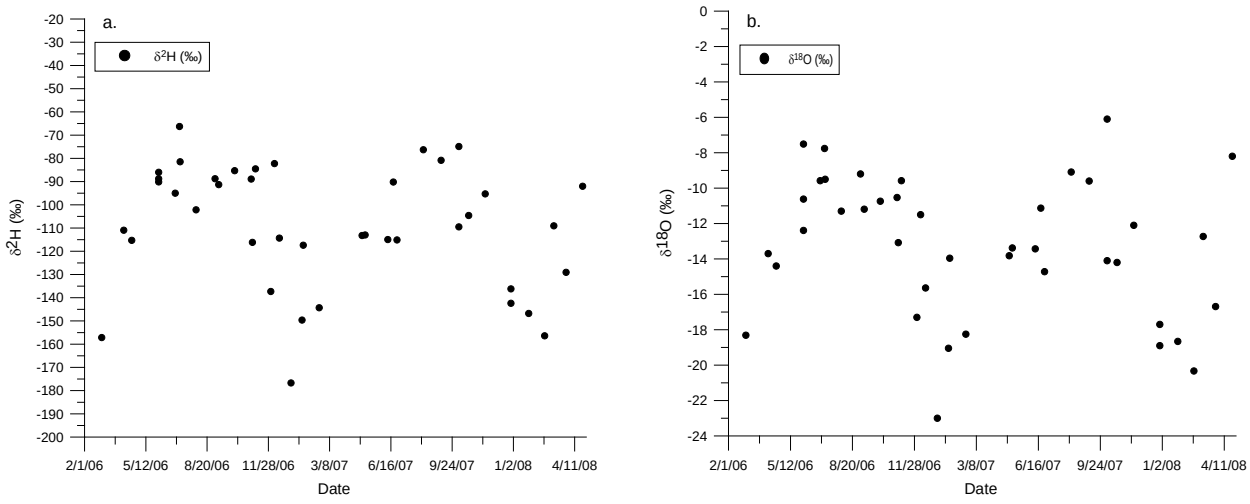

Figure 3.2. a. Seasonal pattern in δ^2H values of precipitation samples collected in the Okanagan Basin, BC, Canada, between April 2006 and April 2008. b. Seasonal pattern in $\delta^{18}O$ values of precipitation samples collected in the Okanagan Basin between April 2006 and April 2008.

The evolution towards more depleted values eastward from Victoria to Calgary may be controlled in part by Rayleigh fractionation processes, where vapour masses originating in the Pacific Ocean became depleted in ^2H and ^{18}O as they moved over the Coast Ranges located west of the Georgia Strait (*i.e.*, Vancouver Island and the Olympic Mountains). Upon reaching the Georgia Strait, recycling of water occurred as the residual water vapour became isotopically enriched by re-evaporation of the ocean surface (Yonge et al., 1989). As the vapour mass continued its movement east over mountain ranges and across the continent towards the Continental Divide, both the continental and altitude effect imparted a progressive depletion in

^{2}H and ^{18}O. These effects, however, were not sufficient to explain the observed relationship between $\delta^{2}H$ and $\delta^{18}O$ values of precipitation in the Okanagan Basin.

3.4.1.2 Spatial Trends in the Isotopic Composition of Precipitation

In five of the seven precipitation sample sets collected concurrently from West Osoyoos and West Kelowna, the $\delta^{2}H$ and $\delta^{18}O$ values of precipitation samples from West Kelowna were more enriched than those of precipitation samples from West Osoyoos. The difference in isotopic compositions of precipitation from West Osoyoos and West Kelowna was not related to predictable isotopic fractionation processes. For example, the dataset did not suggest that secondary evaporation was more prominent in Osoyoos where evapotranspiration rates were slightly higher than those of Kelowna. Nor did the dataset suggest that precipitation falling in

Table 3.2. Summary of $\delta^{2}H$ and $\delta^{18}O$ values in precipitation and corresponding $\delta^{2}H$-$\delta^{18}O$ linear regression equations for Osoyoos (West [W], East [E] and pooled data) and West Kelowna, and for Victoria (Fritz et al., 1987), Calgary (Peng et al., 2004), the Canadian Meteoric Water Line (CMWL) (Fritz et al., 1987) and Global Meteoric Water Line (GMWL) (Craig, 1961).

Station	Time Period	Avg. $\delta^{2}H$ value (‰)	Amount-weighted annual $\delta^{2}H$ value (‰)	Avg. $\delta^{18}O$ value (‰)	Amount-weighted annual $\delta^{18}O$ value (‰)	$\delta^{2}H/\delta^{18}O$ linear regression equation	R^{2}
Osoyoos W	2006-2008	-112	-109	-13.4	-13.5	$\delta^{2}H=5.82\delta^{18}O-34.17$	0.94
Osoyoos E	2006-2008	-104	-102	-11.9	-11.4	$\delta^{2}H=6.82\delta^{18}O-23.00$	0.84
Osoyoos (pooled data)		-110		-12.9		$\delta^{2}H=6.06\delta^{18}O-31.21$	
			-106		-12.7	$\delta^{2}H=6.00\delta^{18}O-32.04$	0.93
W Kelowna	2006-2008	-108		-13.6		$\delta^{2}H=7.03\delta^{18}O-12.68$	0.97
			-107		-13.5	$\delta^{2}H=7.18\delta^{18}O-10.69$	0.99
Victoria: 48.65°N, 23.43°W 20masl	1975-1982		-77		-10.2	$\delta^{2}H=7.49\delta^{18}O-1.56$	0.86
Calgary: 51.01°N, 14.01°W 1049masl	1992-2001		-136		-17.9	$\delta^{2}H=7.68\delta^{18}O-0.21$	0.96
CMWL						$\delta^{2}H=7.75\delta^{18}O+9.83$	
GMWL						$\delta^{2}H=8\delta^{18}O+10$	

Kelowna was more depleted in ^{2}H and ^{18}O as vapour masses moved northward from the south Okanagan Basin to the north Okanagan Basin, and to a higher elevation. Additional samples collected concurrently from both stations may aid in resolving this difference.

3.4.2 $\delta^{2}H$-$\delta^{18}O$ Relationship

The $\delta^{2}H$ and $\delta^{18}O$ values of precipitation collected from the Okanagan Basin between April 2006 and April 2008 are plotted on a $\delta^{2}H$-$\delta^{18}O$ diagram (Figure 3.3). Minimum values plot on the lower left side of the $\delta^{2}H$-$\delta^{18}O$ diagram and correspond to winter precipitation, while maximum values plot on the upper right side of the $\delta^{2}H$-$\delta^{18}O$ diagram and correspond to summer/early fall precipitation. Winter precipitation values plot closer to the GMWL than do late spring and summer rains, as in Gammons et al. (2006) and as described in Clark and Fritz (1997), as a result of "effects" (*i.e.*, temperature, evaporation).

The LMWLs for Osoyoos and West Kelowna using individual $\delta^{2}H$ and $\delta^{18}O$ values were represented by equation $\delta^{2}H = 6.06\delta^{18}O–31.21$ for Osoyoos and by equation $\delta^{2}H = 7.03\delta^{18}O–12.68$ for West Kelowna (Figure 3.3). The Osoyoos LMWL and the West Kelowna LWML exhibited a slightly lower slope and a considerably lower intercept than those of the GMWL, CMWL, and the LMWLs of Victoria and Calgary. LMWLs generated with individual sample values of $\delta^{2}H$ and $\delta^{18}O$ generally have shallower slopes and lower intercepts than LMWLs generated with amount-weighted monthly average $\delta^{2}H$ and $\delta^{18}O$ values (Peng et al., 2004). However, the lower slopes and intercepts of the LMWLs for Osoyoos and West Kelowna were largely a function of the "effects" on late spring and summer rains.

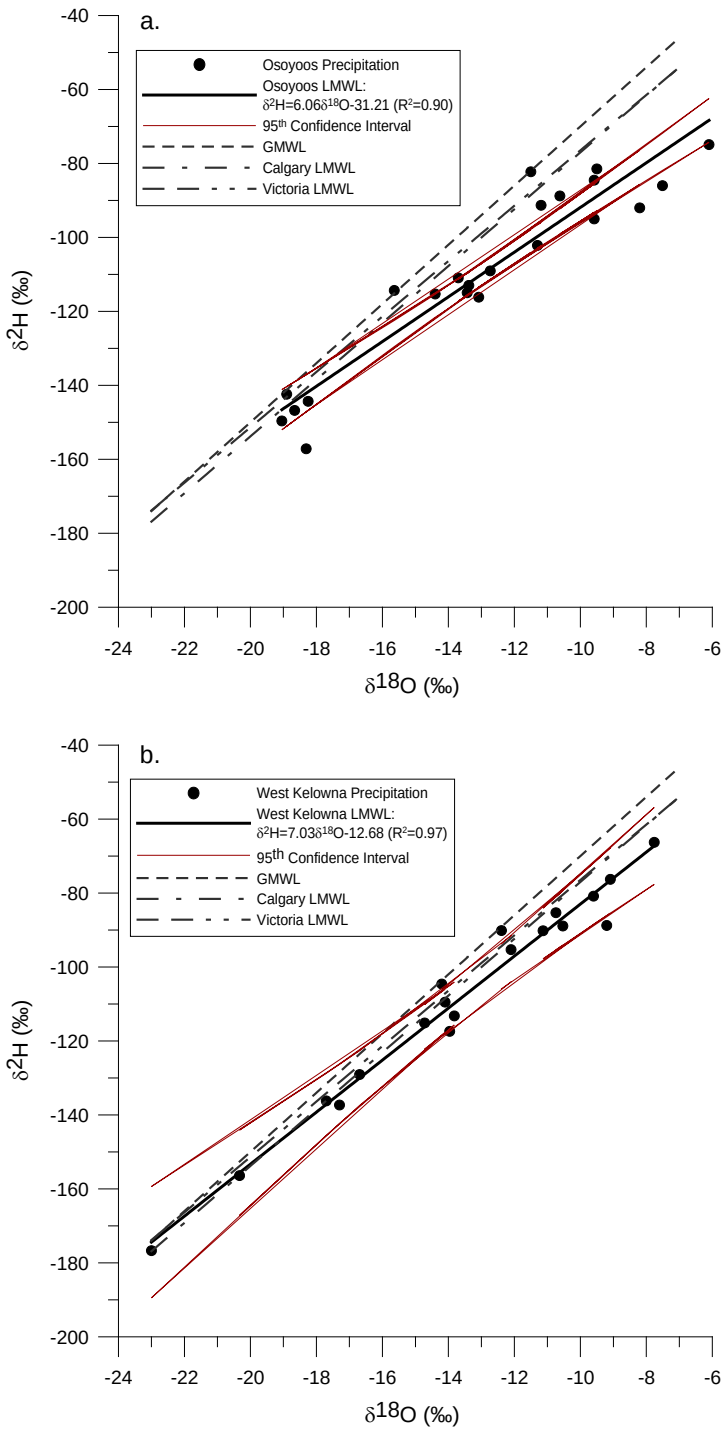

Figure 3.3. a. δ^2H-$\delta^{18}O$ diagram showing δ^2H and $\delta^{18}O$ values of precipitation samples collected in Osoyoos, British Columbia, Canada, between April 2006 and April 2008, and the linear regression equation and 95th confidence interval of the regression line. b. δ^2H-$\delta^{18}O$ diagram showing δ^2H and $\delta^{18}O$ values of precipitation samples collected in West Kelowna, British Columbia, Canada, between April 2006 and April 2008, and the linear regression equation and 95th confidence interval of the regression line. LMWLs for Victoria (Fritz et al., 1987) and Calgary (Peng et al., 2004) and GMWL (Craig, 1961) are shown for comparison.

The individual δ^2H and $\delta^{18}O$ values of winter precipitation (November to April) and of summer precipitation (May to October) collected from Osoyoos and West Kelowna are plotted separately on a δ^2H-$\delta^{18}O$ diagram (Figure 3.4). Linear regression was completed for the winter dataset and summer dataset of each station. Seasonally, the regression lines for Osoyoos were represented by equation $\delta^2H = 6.44\delta^{18}O–25.01$ for winter and by equation $\delta^2H = 5.39\delta^{18}O–38.67$ for summer. Seasonal regression lines for West Kelowna were represented by equation $\delta^2H = 6.70\delta^{18}O–20.47$ for winter and by equation $\delta^2H = 5.83\delta^{18}O–25.07$ for summer. The slopes and intercepts of summer precipitation were notably lower than those of the winter precipitation (Figure 3.4). The lower slopes and intercepts were attributed to four "effects": temperature, primary evaporation, secondary evaporation and weather systems, as discussed in detail in Sections 3.5.2.1 through 3.5.2.4. Note that Yonge et al. (1989) indicated that evapotranspiration

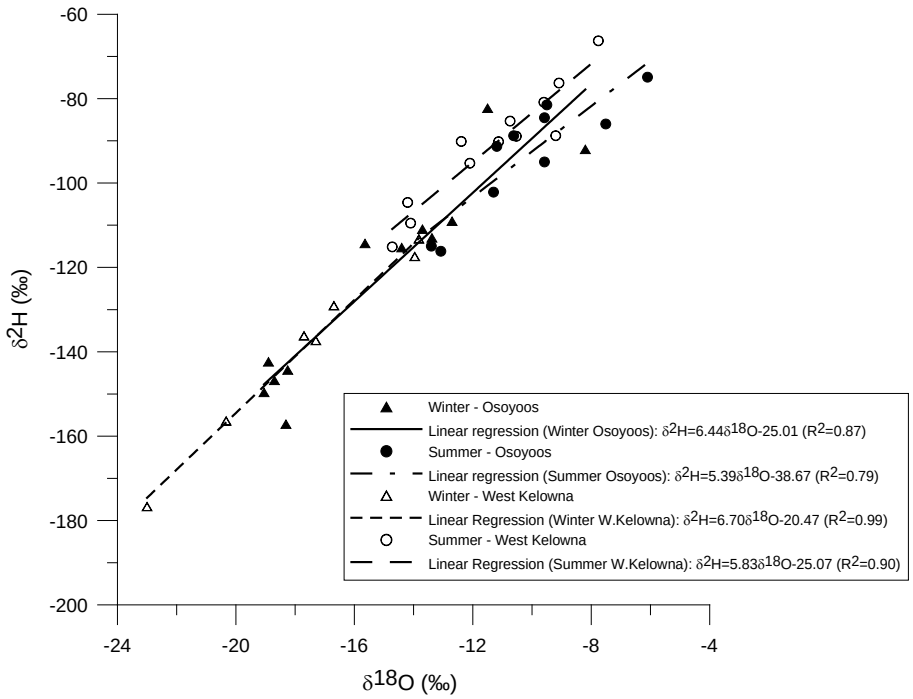

Figure 3.4. δ^2H-$\delta^{18}O$ diagram showing δ^2H and $\delta^{18}O$ values of winter precipitation samples (November to April) and of summer precipitation samples (May to October) collected in the Okanagan Basin, British Columbia, Canada, between April 2006 and April 2008, and the corresponding linear regression equations.

and/or other modifying effects did not appear to be occurring in the southern Interior region of British Columbia. The flat gradient measured for the region (-0.8‰/100 km for ^{2}H; -0.6‰/100 km for ^{18}O) was interpreted in terms of temperature and orographic effects and was attributed to a significant reduction in the Rayleigh fractionation process in an area of minimal precipitation (Yonge et al., 1989). However, as data was collected in December only, the lack of seasonal data likely prevented the effects of evapotranspiration and recycling of water vapour from being addressed.

3.4.2.1 Temperature

With an increase in air temperature, the ratio of the isotopic equilibrium fractionation factors of ^{2}H and ^{18}O for water condensation, and thereby, the slope, decrease slightly (Majoube, 1971). Peng et al. (2004) showed that slope and intercept decreased continuously with increasing air temperature by calculating correlation equations between $\delta^{2}H$ and $\delta^{18}O$ values in precipitation at Calgary for different surface air temperature ranges. However, this relationship is generally not enough to cause such variations in slope (Peng et al., 2004).

3.4.2.2 Primary Evaporation

Water vapour that has evaporated from inland surface water bodies and soils in continental areas, particularly in warm seasons, can mix with air masses moving over these areas. Incorporation of this enriched recycled water vapour results in a lower slope (Peng et al., 2004). In semi-arid regions, precipitation from thunderstorms that derive their moisture mainly from local evapotranspiration produce low slopes (Peng et al., 2004). Ingraham and Taylor (1986) showed that subsequent rains downwind from where an air mass receives recycled water vapour will be more enriched in ^{2}H and ^{18}O than if rainout occurred without the addition of recycling water vapour. Water vapour that has transpired from plants can also mix with air

masses, however, transpiration does not produce significant isotopic fractionation (Wershaw et al., 1966). In the Okanagan Basin, summer months are characterized by high evapotranspiration rates, high air temperatures and low relative humidity. These conditions drive evaporation of the Okanagan River system, other smaller surface water bodies, and irrigated soils. The evaporated moisture plays a key role in controlling summer precipitation events (*i.e.*, thunderstorms) and replenishing atmospheric water vapour. The low slope of the regression equations for the Okanagan Basin, particularly the summer equation, may indicate that precipitation contains more local recycled water as a result of incorporation of moisture from evaporation of surface water bodies and irrigated soils.

3.4.2.3 Secondary Evaporation

Secondary evaporation occurs in arid to semi-arid climates where raindrops beneath the cloud-base evaporate as they fall to the ground surface and undergo subsequent isotopic fractionation that decreases the slope (Dansgaard, 1964). During light rain or in rain from the early part of a storm, the rain falling to the ground is more enriched in ^{2}H and ^{18}O as it evaporates during its descent through air of low relative humidity ("amount effect") (Ingraham, 1998; Peng et al., 2004). Once the air below the cloud-base becomes saturated, as it does during the latter part of a storm or in heavy rainstorms, the rain reaching the ground is less enriched in ^{2}H and ^{18}O as evaporation of the raindrops is reduced (Ingraham, 1998). Peng et al. (2004) observed this effect for small rain events of <5 mm and for thunderstorms (>10 mm of rain) that derive their moisture mainly from local evapotranspiration. This effect is generally observed for slopes of summer meteoric water lines, as secondary evaporation of snowfall in the winter is negligible (Fritz et al., 1987). Secondary evaporation during small rain events in the summer may also contribute to the low slope of the summer regression equation for the Okanagan Basin.

3.4.2.4 Weather Systems

Differences in slope and intercept of summer and winter regression equations for the Okanagan Basin may be due to the seasonal difference in the origin of precipitation (*i.e.*, Maritime Polar air mass in the winter and convective systems in the summer).

3.4.3 δ^2H-$\delta^{18}O$ Relationship (Amount-Weighted Values)

The calculated amount-weighted (approximate) monthly δ^2H and $\delta^{18}O$ values of precipitation collected from Osoyoos (West and East) and West Kelowna between April 2006 and April 2008 are presented in Table A-3 of Appendix A, and plotted on a δ^2H-$\delta^{18}O$ diagram (Figure 3.5). Linear regression was completed for each dataset using amount-weighted δ^2H and $\delta^{18}O$ values over an approximate monthly interval to define the linear regression equation (or LMWL) for that station. The LMWLs for Osoyoos and West Kelowna using amount-weighted (approximate) monthly δ^2H and $\delta^{18}O$ values were represented by equation $\delta^2H = 6.00\delta^{18}O–32.04$ for Osoyoos and by equation $\delta^2H = 7.18\ \delta^{18}O–10.69$ for West Kelowna (Figure 3.5). The LMWLs for Osoyoos and West Kelowna using amount-weighted (approximate) monthly δ^2H and $\delta^{18}O$ values were similar to those generated with individual δ^2H and $\delta^{18}O$ values. However, the LMWL for West Kelowna using amount-weighted (approximate) monthly δ^2H and $\delta^{18}O$ values exhibited a slightly higher slope and intercept. This may be a function of (1) a small dataset; and/or (2) where sampling intervals spanned more than one month, data were combined.

3.4.4 Deuterium Excess Values

D-excess values of precipitation samples collected in the Okanagan Basin were tabulated using Equation 2.4 (Table A-1 of Appendix A). D-excess values ranged between -26.4‰ and +10.8‰ (average of -4.9‰ ± 10.8) for West Osoyoos; -25.9‰ and +9.8‰ (average

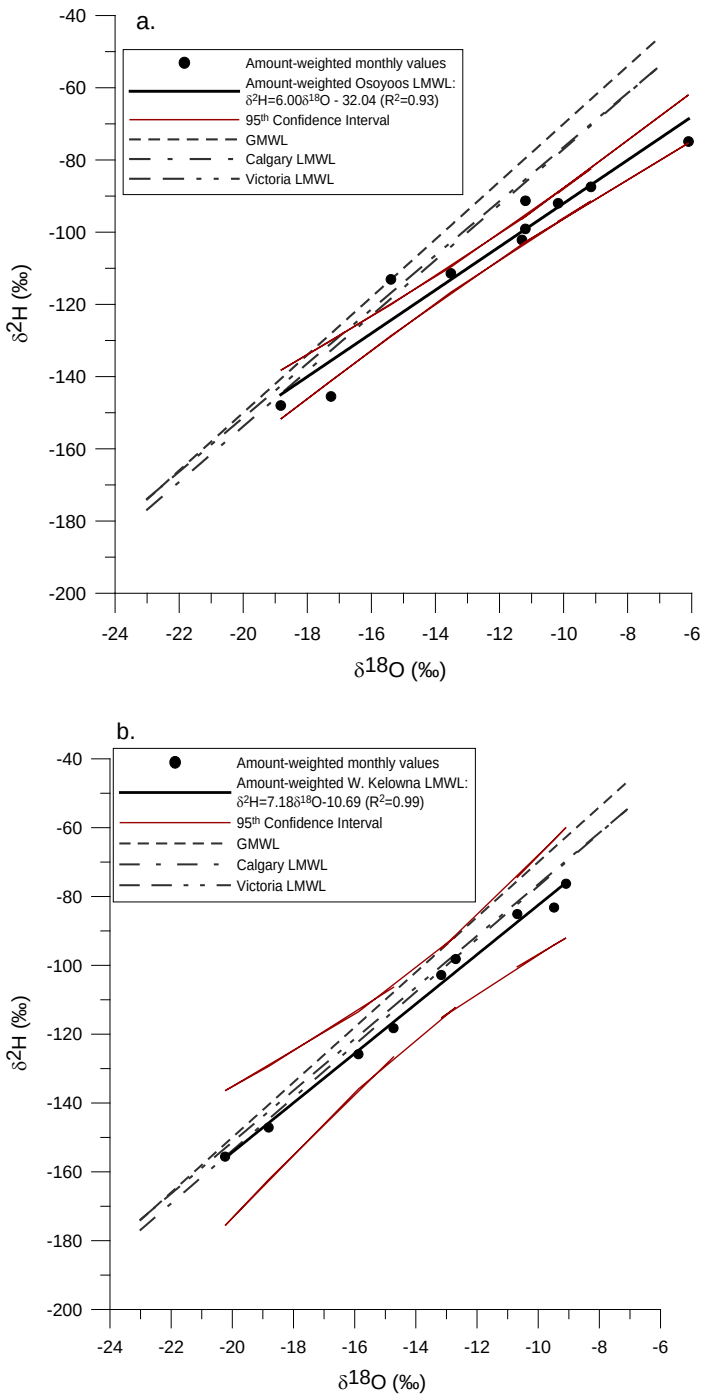

Figure 3.5. a. δ^2H-$\delta^{18}O$ diagram showing amount-weighted (approximate) monthly δ^2H and $\delta^{18}O$ values of precipitation samples collected in Osoyoos, British Columbia, Canada, between April 2006 and April 2008, and the linear regression equation and 95th confidence interval of the regression line. b. δ^2H-$\delta^{18}O$ diagram showing amount-weighted (approximate) monthly δ^2H and $\delta^{18}O$ values of precipitation samples collected in West Kelowna, British Columbia, Canada, between April 2006 and April 2008, and the linear regression equation and 95th confidence interval of the regression line. LMWLs for Victoria (Fritz et al., 1987) and Calgary (Peng et al., 2004) and GMWL (Craig, 1961) are shown for comparison.

of -8.8‰ ± 11.5) for East Osoyoos; and -15.2‰ and +9.0‰ (average of 0.5‰ ± 6.1) for West Kelowna. D-excess values were lowest in the summer/early fall and highest in the winter, as shown on Figure 3.6. In general, negative d-excess values were calculated for summer months, while positive d-excess values were calculated for winter months. The four precipitation samples from Osoyoos West that exhibited more positive δ^2H and $\delta^{18}O$ values than all other samples collected during this study had d-excess values of between -26.2 to -76.8 ‰. The d-excess values for these samples were greater than one to two standard deviations of the mean (Table A-1 of Appendix A), further indicating that the samples were outliers.

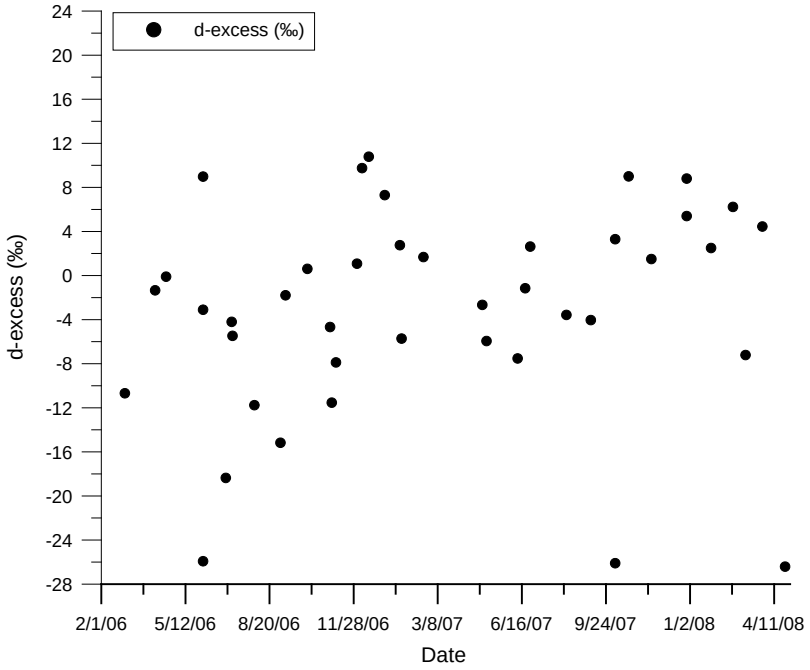

Figure 3.6. Seasonal pattern in d-excess values of precipitation samples collected in the Okanagan Basin, BC, Canada, between April 2006 and April 2008.

D-excess values for precipitation in the Okanagan Basin could not be explained by meteorological conditions at the source region of the vapour mass alone (*i.e.*, relative humidity, wind speed and temperature). Low to negative d-excess values for precipitation in the Okanagan Basin, particularly during the summer, reflected secondary processes identified above:

1) incorporation of local recycled water vapour into the air mass; and 2) secondary evaporation of rainfall during small rain events. The variable d-excess values during winter (generally -11 to +11‰) may have reflected high humidity during formation of Pacific vapour masses (for low d-excess values) and non-equilibrium conditions that occurred during the formation of snow (for high d-excess values) (Merlivat and Jouzel, 1979). The differences in d-excess values between summer and winter precipitation in the Okanagan Basin may have been due in part to the different origins of moisture: westerly air masses in winter and localized convective systems in summer.

3.4.5 δ^{18}O-Temperature Relationship

The individual δ^{18}O values of precipitation collected from Osoyoos and West Kelowna between April 2006 and April 2008 and the average temperature (T) for the (approximate) monthly sampling interval are plotted on a δ^{18}O-Temperature diagram (Figure 3.7). As with the IAEA GNIP network, the average temperature includes time at which no precipitation occurred. The relationship between δ^{18}O values and average temperature was $T = 0.32\delta^{18}O–15.95$ for Osoyoos and $T = 0.40\delta^{18}O–17.77$ for West Kelowna. The isotopic depletion in ^{18}O per one degree drop in temperature was about -0.3 to -0.4‰.

3.5 Summary and Conclusions

The stable isotope compositions of ^{2}H and ^{18}O were evaluated for precipitation collected in the Okanagan Basin (specifically, Osoyoos and Kelowna) between April 2006 and April 2008. A seasonality between temperature and the isotopic composition of precipitation was evident, where minimum values occurred in the winter and maximum values occurred in the summer. Average annual δ^{2}H and δ^{18}O values were -112‰ and -13.4‰, respectively, at Osoyoos West, -104‰ and -11.9‰, respectively, at Osoyoos East, and -108‰ and -13.6‰, respectively, at

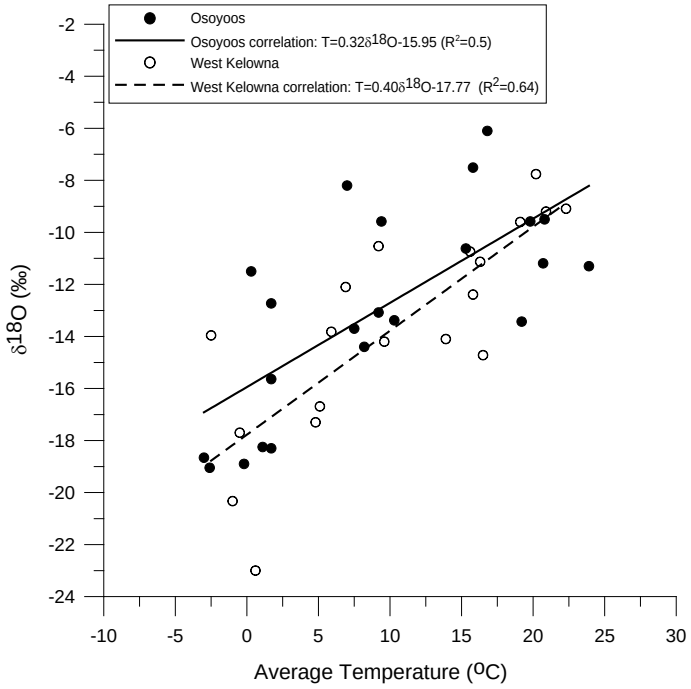

Figure 3.7. $\delta^{18}O$-Temperature diagram showing $\delta^{18}O$ values of precipitation samples for Osoyoos and West Kelowna between April 2006 and April 2008 plotted against average temperature for each sampling interval.

West Kelowna. Amount-weighted annual $\delta^{2}H$ and $\delta^{18}O$ values were -109 and -13.5‰, respectively, at Osoyoos West; -102 and -11.4‰, respectively, at Osoyoos East; and -107 and -13.5‰, respectively, at West Kelowna.

Average and amount-weighted annual $\delta^{2}H$ and $\delta^{18}O$ values of precipitation in the Okanagan Basin were more depleted than $\delta^{2}H$ and $\delta^{18}O$ values of precipitation in Victoria, and more enriched than $\delta^{2}H$ and $\delta^{18}O$ values of precipitation in Calgary. This progressive depletion in ^{2}H and ^{18}O was controlled in part by Rayleigh fractionation, where moisture was removed from maritime Pacific air masses by the continental and altitudinal effect as they moved eastward from the Pacific Ocean to the Continental Divide. Using individual $\delta^{2}H$ and $\delta^{18}O$ values, the LWML for Osoyoos (West and East) was $\delta^{2}H=6.06\delta^{18}O–31.21$ and the LWML for West Kelowna was $\delta^{2}H=7.03\delta^{18}O–12.68$. Using amount-weighted (approximate) monthly $\delta^{2}H$ and

$\delta^{18}O$ values, the LWML for Osoyoos (West and East) was $\delta^{2}H=6.00\delta^{18}O-32.04$ and the LWML for West Kelowna was $\delta^{2}H=7.03\delta^{18}O–10.69$. The slope and intercept of the summer regression lines for Osoyoos and West Kelowna using individual $\delta^{2}H$ and $\delta^{18}O$ values were lower than those of the winter regression lines for Osoyoos and West Kelowna, indicative that summer precipitation was affected by secondary processes such as recycling (mixing) of water vapour and secondary evaporation of raindrops. Seasonal variation in the origin of precipitation (*i.e.*, Maritime Polar air mass in the winter and convective systems in the summer) may also have played a role in controlling the slope and intercept of the regression lines.

The addition of at least one more precipitation sampling station (*i.e.*, in the north portion of the Okanagan Basin) would provide more detailed information on temporal and spatial variations on the isotopic composition of precipitation throughout the Okanagan Basin, as well as information on the effect that seasonal weather systems have on the isotopic composition of precipitation in the Okanagan Basin.

3.6 Acknowledgements

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CHAPTER 4
STABLE ISOTOPES OF HYDROGEN AND OXYGEN IN SURFACE WATERS IN THE OKANAGAN BASIN, BRITISH COLUMBIA, CANADA

Abstract. Stable isotopes of hydrogen and oxygen in surface waters can be used to characterize processes (mixing, residence, recharge source[s]) in surface waters. In semi-arid environments, the isotopic composition of ^{2}H and ^{18}O in surface waters can be used to assess whether surface evaporation has occurred. In the Okanagan Basin of British Columbia, Canada, the Okanagan River system is a vital source of water for multiple stakeholders. This study was conducted to compare the isotopic composition of the Okanagan River system waters to that of precipitation in the Okanagan Basin, and to evaluate the isotope characteristics and dynamics of the Okanagan River system. 140 samples were collected on a monthly basis from May 2006 to April 2008 at 10 locations along the Okanagan River system and, for comparison, at 11 isolated surface water bodies in the South Okanagan Basin. Results showed that $\delta^{2}H$ and $\delta^{18}O$ values ranged from -111 to -98‰ and -13.5 to -8.9‰, respectively. The data suggested that the Okanagan River system behaved as a single hydrologic unit, with Okanagan Lake being the source of water exiting the Basin. Minimum $\delta^{2}H$ and $\delta^{18}O$ values occurred in the spring, likely from recharge by snowmelt and spring rains; maximum values occurred in the fall, indicative of evaporation. Peak $\delta^{2}H$ and $\delta^{18}O$ values in late fall followed closely by decreasing values was indicative of turnover and mixing with deeper waters. $\delta^{2}H$ and $\delta^{18}O$ values of the Okanagan River system were more positive than those of Okanagan Basin precipitation, plotting to the right of local meteoric water lines for Osoyoos and West Kelowna, and suggested evaporation of surface waters. Assuming evaporation took place during storage and within watershed creeks and tributaries prior to waters entering Okanagan Lake, up to 32% of water was lost to evaporation. The theoretical equation for the local evaporation line of the Okanagan River system was $\delta^{2}H=5.41\delta^{18}O–41.15$. $\delta^{2}H$ and $\delta^{18}O$ values of 11 isolated surface water bodies were generally different than those of the Okanagan River system, with each water body exhibiting a varying degree of evaporation.

Key Words: surface water, isotopes, semi-arid, evaporation, local evaporation line, lake mixing.

4.1 Introduction

Surface waters are complex dynamic systems connected to the water cycle through surface and subsurface recharge and discharge, and via precipitation-evaporation fluxes (Froehlich et al., 2005). The application of the isotopic tracers ^{2}H and ^{18}O in surface water studies have been used to assess numerous environmental issues, including water balance of lakes and surface reservoirs (Gibson, 2002; Gibson and Edwards, 2002; Longinelli et al., 2008; Wolfe et al., 2007), lake and river dynamics (Ferguson et al., 2007; Gibson et al., 2002; Kendall and Coplen, 2001; Pham et al., 2009; Rock and Mayer, 2007), surface water–groundwater interactions (Gammons et al., 2006), and palaeohydrologic and palaeoclimatological problems (Yu et al., 2002). Gibson et al. (2005) provide an overview of studies conducted in Canada involving the ^{2}H and ^{18}O isotopes of surface waters.

The isotopic composition of ^{2}H and ^{18}O in surface waters in semi-arid environments can be modified by non-equilibrium evaporation, whereby water molecules containing the heavier isotopes are diffused at a lower rate than water molecules containing the lighter isotopes (Clark and Fritz, 1997; Gat, 1981; Gibson et al., 2005; Gonfiantini, 1986). Surface waters that have undergone evaporation are thus more enriched in ^{2}H and ^{18}O than the resulting water vapour (Froehlich et al., 2005). The degree of isotopic enrichment of evaporating surface waters is dependent on meteorological factors, including: atmospheric relative humidity, surface water temperature and salinity (Clark and Fritz, 1997; Gonfiantini, 1986; Rozanski et al., 2001). The isotopic composition of evaporating surface waters evolves along a line at a slope that is less than that of the global and/or local meteoric water lines and that originates at the initial isotopic composition of the water prior to evaporation (Clark and Fritz, 1997; Rozanski et al., 2001). The linear trend exhibited by increasing ^{2}H and ^{18}O is commonly referred to as the local evaporation

line (LEL) (Gibson et al., 2005). The amount of evaporation that has occurred on a given surface water body can be estimated using the Craig and Gordon model (1965), developed for evaluating the isotopic composition of the evaporation flux into an open (unsaturated) atmosphere. Additionally, the evaporation-to-inflow ratio (E/I) can be used to determine the relative influence of evaporation and water inflow on the water balance of a surface water body (Gibson et al., 1996; Gibson, 2002; Wolfe et al., 2007; Ferguson et al.; 2007; Pham et al., 2009).

In semi-arid areas, surface waters can be an important source of water for domestic, irrigation and recreational purposes, as well as for supporting fish and aquatic habitat. In the Okanagan Basin of British Columbia, Canada, the Okanagan River system is one such body. In view of the increasing population in the Basin, growth in the industrial and agricultural sectors, and the potential impacts of climate change, knowledge of the dynamics of surface water resources is critical for their management and protection (BC Ministry of Environment [BC MOE], July 2008a). Several local-scale research projects that incorporate the analysis of ^{2}H and ^{18}O of surface waters are currently being conducted in parts of the basin (Neilson-Welch and Allen, 2007). However, there are no known regional-scale studies currently being conducted on the isotopic composition of surface waters of the Okanagan Basin, particularly within the Okanagan River system, nor on the amount of water within the Okanagan River system that is lost to evaporation. The objectives of this study were to: (1) compare the isotopic composition of surface waters, in particular, those of the Okanagan River system, to that of local precipitation in the Okanagan Basin and (2) evaluate the isotopic characteristics and dynamics of the Okanagan River system, including whether $\delta^{2}H$ and $\delta^{18}O$ values become systematically positive in a downstream direction as a result of a warmer and drier climate at the south end of the Basin; and an estimate of the fraction of water loss by evaporation.

4.2 Study Area

4.2.1 Location

The Okanagan Basin is located in the Southern Interior Plateau of British Columbia and northern Washington (in the United States). The Basin lies in a north-south trending valley and includes all lands surrounding streams and lakes that discharge into the Okanagan River (Figure 4.1). Within British Columbia, the Okanagan Basin extends for roughly 160km, from Armstrong (just north of Vernon) in the north to the Canada-United States border (at Osoyoos) in the south, and covers an area of approximately 8,200 km^2. This portion of the Basin consists of a main trench, and a secondary trench to the east that parallels the main trench. The Okanagan Basin extends for roughly 115 km south into the United States. It is important to note that the Similkameen Basin lies adjacent to the west side of the Okanagan Basin and includes all lands surrounding streams and lakes that ultimately discharge into the Similkameen River (Figure 4.1). The Similkameen River enters the Okanagan River at Oroville, United States. This study is focused only on the portion of the Okanagan Basin located in Canada, with supplementary data from Oroville, United States (not including the Similkameen Basin or Similkameen River).

4.2.2 Okanagan River System

The Okanagan Basin is comprised of six large lakes: Wood, Kalamalka, Okanagan, Skaha, Vaseaux and Osoyoos lakes, and their tributaries (Figure 4.1). Wood and Kalamalka Lake are located east of Okanagan Lake, and flow north prior to discharging into the Vernon arm of Okanagan Lake. They do not form part of this study and are not discussed further in this report. Okanagan, Skaha, Vaseaux and Osoyoos lakes flow south. The physical characteristics of the lakes in the main trench are summarized in Table 4.1. The Okanagan River begins at the outlet of Okanagan Lake and flows through Skaha, Vaseaux and Osoyoos Lakes before joining

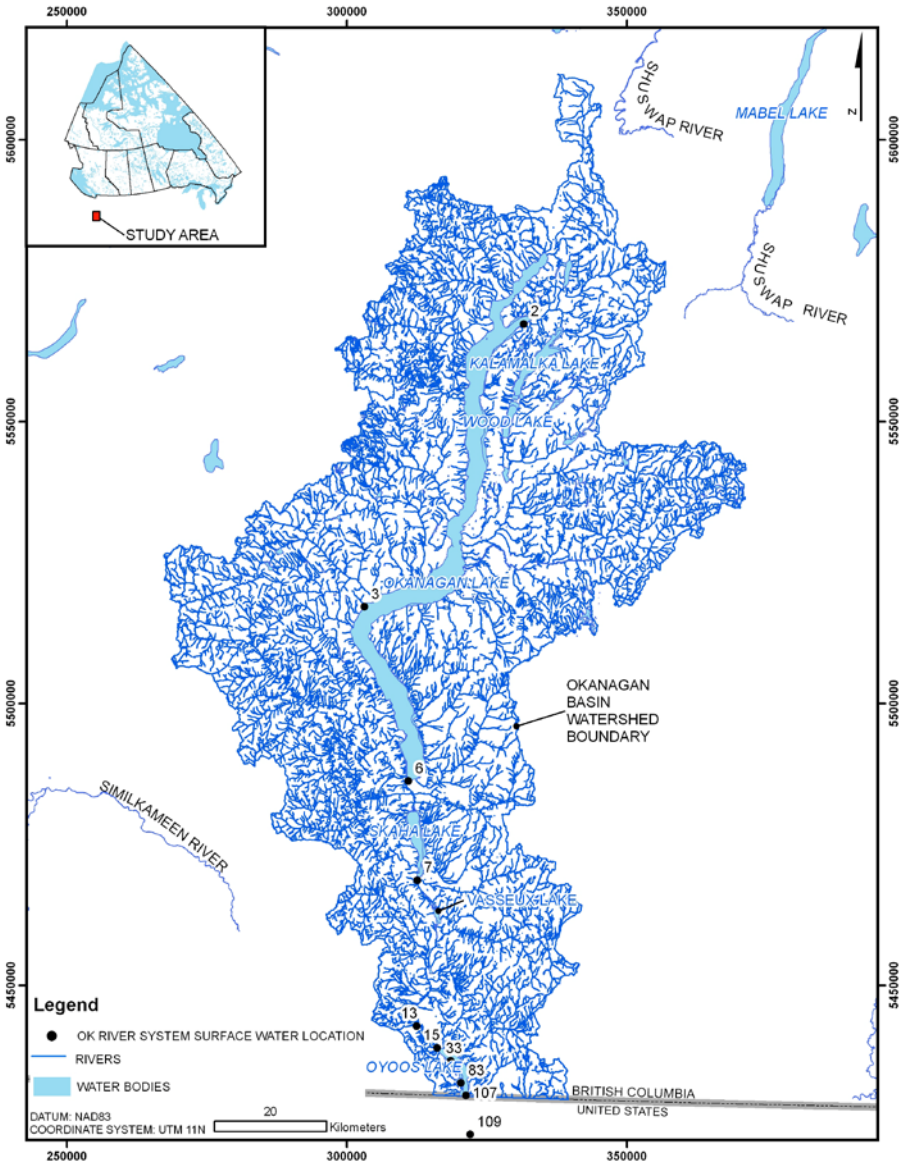

Figure 4.1. Map showing location of Okanagan Basin within British Columbia, Canada, and locations of surface water collection stations (numbers) along the Okanagan River system. Map produced using river data from the website www.geobase.ca (National Hydro Network, station 08nm001) and national boundary line and water body data from DMTI Spatial Inc.

Table 4.1. Physical characteristics of lakes in the main trench of the Okanagan Basin, British Columbia, Canada (Jensen, 2007; Rae, 2005; Stockner and Northcote, 1974).

Lake	Length (km)	Surface Area (km^2)	Volume (km^3)	Mean Depth (m)	Maximum Depth (m)	Water Residence Time (years)
Okanagan	113	344	24.6	76	242	53 to 60
Skaha	12	20	0.6	26	57	1.2
Vaseaux	4	2.8	0.02	6.5	27	0.03 (~15 wks)
Osoyoos	16	23	0.4	14	63	0.7 (~36 wks)

the Columbia River in Washington, United States. Nearly 0.5 km^3 of water has been estimated to flow through the Okanagan River each year (Rae, 2005). Most of the discharge that exits the Okanagan Basin originates above the outlet of Okanagan Lake (Merritt and Alila, 2004). The Okanagan River has been significantly modified by irrigation and flood control dams, channelization, river flow containment dykes and vertical drop structures (Osoyoos Lake Water Quality Society, July 2008). Nearly 200 water licenses have been allocated along the Okanagan River for irrigation, waterworks, domestic, land improvement and storage purposes (BC Ministry of Environment [BC MOE], July 2008b).

Discharge and water levels are recorded at hydrometric stations along the Okanagan River at the Okanagan Lake outlet dam in Penticton, the Skaha Lake outlet dam in OK Falls, and the vertical drop structure between Oliver and Osoyoos (Environment Canada [EC], July 2008). For the years 2006 and 2007, discharge was highest during spring (March to June), with a secondary peak during the month of September. High discharge rates during the spring likely correspond to the spring freshet and occasional heavy rains, while peak discharge rates in the fall likely correspond to increased water volumes from Okanagan Lake to meet irrigation requirements for agricultural purposes further south in the Basin. Water levels correlate with discharge, where high water levels are recorded during periods of high discharge. Osoyoos Lake levels are regulated by Zosel Dam, located 4 km south of Osoyoos in the United States.

4.2.3 Climate

The climate of the Okanagan Basin is semi-arid. Mean temperatures increase and precipitation gradually decreases from the north part of the Basin towards the south (EC, February 2008). For most of the year, evapotranspiration generally exceeds precipitation throughout much of the Basin (Farmwest, February 2008).

4.3 Materials and Methods

Water samples (n = 140) were collected on an approximate monthly basis from May 2006 to April 2008 at ten stations along the Okanagan River system (Figure 4.1). A list of stations and their spatial coordinates is provided in Table 4.2. Two stations were located in Okanagan Lake at Ellison and Peachland. Four stations were located in the Okanagan River at Penticton, Okanagan Falls, south of Oliver and Oroville (United States). Four stations were located in Osoyoos Lake: at the mouth of the Okanagan River, north basin ("pumphouse"), central basin and at the Canada-United States border.

Table 4.2. Spatial coordinates of surface water sampling stations in the Okanagan Basin, British Columbia, Canada.

Station	Station ID	Location	Elevation (masl)
Okanagan River System			
Okanagan Lake			
Ellison	2	50.24°N 119.36°W	345
Peachland	3	49.78°N 119.73°W	345
Okanagan River			
Penticton	6	49.50°N 119.61°W	340
OK Falls	7	49.34°N 119.58°W	340
Oliver	13	49.11°N 119.57°W	280
Oroville, United States	109	48.94°N 119.43°W	280
Osoyoos Lake			
Mouth of River	15	49.08°N 119.52°W	280
Pumphouse	33	49.06°N 119.48°W	280
Central Basin	83	49.02°N 119.46°W	280
Canada-United States Border	107	49.00°N 119.44°W	280
Other Surface Water Bodies			
McKinney Creek	14	49.12°N 119.19°W	1086
Spotted Lake	21	49.08°N 119.57°W	572
Kettle Lake	49	49.05°N 119.49°W	287
Wildhorse	51	49.05°N 119.55°W	864
Blue Lake	55	49.04°N 119.56°W	852
Peanut Pond	63	49.03°N 119.47°W	283
Kilpoola Lake	67	49.03°N 119.56°W	821
Taylor	69	49.03°N 119.40°W	850
Chapman	75	49.03°N 119.39°W	842
Haynes Creek	99	49.01°N 119.40°W	749
Yos Pond	105	49.01°N 119.25°W	1354

For comparison, six surface water samples were collected between May and September 2006 from two surface water bodies in the south Okanagan that did not appear to be

hydraulically connected to the Okanagan River system: Peanut Pond and an unnamed kettle lake, both located in Osoyoos. Four surface water samples were collected in May 2006 and October 2007 at Spotted Lake, Wildhorse, Kilpoola Lake and Blue Lake located northwest of Osoyoos on Kilpoola Mountain. Four surface water samples were collected in April and May 2006 at Haynes Creek, Chapman and Taylor, and in September 2008 at Yos Pond, located east of Osoyoos on Anarchist Mountain. One surface water samples was collected in September 2008 from McKinney Creek on Mt. Baldy, east of Oliver. These surface water locations are shown on Figure 4.2. A list of stations and their spatial coordinates is provided in Table 4.2.

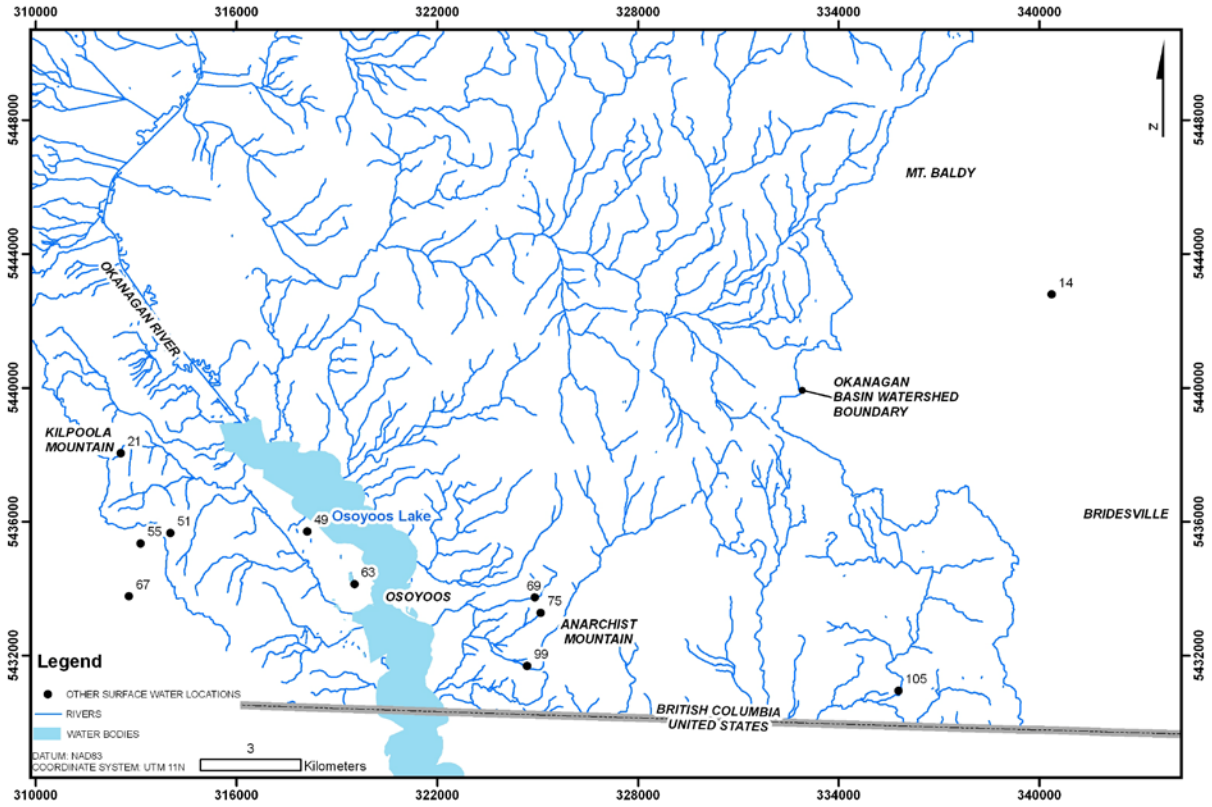

Figure 4.2. Map showing locations of other surface water collection stations in the South Okanagan Basin, British Columbia, Canada. Map produced using river data from the website www.geobase.ca (National Hydro Network, station 08nm001) and national boundary line and water body data from DMTI Spatial Inc.

Unfiltered surface water samples were collected by hand, bucket or bailer, with the exception of samples from Osoyoos Lake, which were collected from a boat using a Van Dorn sampler, and two samples from the kettle lake (samples 2 and 3), which were collected directly from a hose connected to a pump within the lake. Water samples were collected in 4 to 30 ml high density polyethylene (HDPE) bottles and filled so that no, to minimal, headspace remained. All surface water samples were collected at a depth of up to 0.3 m below the top of the water surface, with the exception of two samples from the kettle lake (2 and 3) which were collected from a pump at an undetermined depth below the water surface. Field pH and temperature were measured at the time of sample collection using an ORION 250A+ pH and temperature probe. Alkalinity was measured by titration to an endpoint of pH 4.6 shortly after sample collection using a Hach alkalinity kit with a digital titrator.

Water samples were analyzed for δ^2H and $\delta^{18}O$ at Environment Canada's National Hydrology Research Center (NHRC) in Saskatoon, SK. Sample analysis was conducted on isotope ratio mass spectrometers (IRMS) between April 2006 and April 2007 and by laser spectroscopy (Lis et al., 2008) between April 2007 and April 2008. Where IRMS was used, δ^2H values were measured by converting the water sample into H_2 gas using the standard Zn reduction technique (Coleman et al., 1982) and $\delta^{18}O$ values were measured using the standard CO_2-water equilibration technique (Epstein and Mayeda, 1953). Results were reported relative to VSMOW in the δ(‰) notation (Equation 2.1). The error in the reported values was ±2.0‰ (IRMS) or ±1.0‰ (laser spectroscopy) for δ^2H and ±0.2‰ for $\delta^{18}O$.

4.3.1 Other Work

Six samples were collected in May, July and September 2006 at two Town of Osoyoos pumphouses that draw water from the bottom of Osoyoos Lake. The pumphouses are located

along the shore of Osoyoos Lake, directly west of surface water stations "pumphouse" and "central basin". The samples were collected as part of work completed for this study to satisfy a component of Objective 1 (Regional Hydrogeology of the South Okanagan Basin), as described in Chapter 5 of this thesis. Samples were submitted to NHRC for analysis of δ^2H and $\delta^{18}O$ values using the isotope ratio mass spectrometer, as described above. The δ^2H and $\delta^{18}O$ values of these deeper water samples from Osoyoos Lake were used in this Chapter to compare to the δ^2H and $\delta^{18}O$ values in shallow water samples from Osoyoos Lake.

Sixty groundwater samples were collected in the highlands of the south Okanagan Basin between April 2006 and September 2008. These samples were collected as part of work completed for this study to satisfy a component of Objective 1 (development of a conceptual hydrogeological model for the South Okanagan Basin), as described in Chapter 5 of this thesis. Samples were submitted to NWRI for analysis of δ^2H and $\delta^{18}O$ values using the isotope ratio mass spectrometer, as described above. The δ^2H and $\delta^{18}O$ values of highland groundwaters were used in this Chapter to develop the local evaporation line (LEL) for the Okanagan River system.

Three surface water samples were collected by BC MOE: one from the Oliver station in February 2006 and two from the Osoyoos Lake Pumphouse station in March 2006. Samples from the Pumphouse station were composites, where Sample 1 represented waters from 1, 5 and 10 m depths, and Sample 2 represented waters from 20, 32 and 45 m depths. Samples were submitted to NWRI for analysis of δ^2H and $\delta^{18}O$ values using the isotope ratio mass spectrometer, as described above.

The local meteoric water lines (LMWL) for Osoyoos and West Kelowna, established in Chapter 3 of this thesis (Stable Isotopes of Hydrogen and Oxygen in Precipitation in the Okanagan Basin), were used for comparison of δ^2H and $\delta^{18}O$ values of surface waters. Using

individual δ^2H and $\delta^{18}O$ values in precipitation, the LMWL for Osoyoos was $\delta^2H=6.06\delta^{18}O-31.21$ and the LWML for West Kelowna was $\delta^2H=7.03\delta^{18}O–12.68$.

4.4 Results and Discussion

4.4.1 Okanagan River System

4.4.1.1 δ^2H and $\delta^{18}O$ Values

The δ^2H and $\delta^{18}O$ values of surface water samples collected along the Okanagan River system between February 2006 and April 2008 are presented in Table B-1 of Appendix B and shown temporally on Figure 4.3. The δ^2H and $\delta^{18}O$ values ranged from -111 to -98‰ (mean of -103 ± 3‰) and -13.5 to -8.9‰ (mean of -11.5 ± 0.7‰), respectively. There was an inverse relationship between the isotopic composition of surface water samples and the time of year, where the lowest (more negative) values occurred in the spring months of May and June, and the highest (more positive) values occurred in the fall months of September and October.

4.4.1.2 Spatial Variations

Surface water samples collected from all sampling stations did not show that isotopic enrichment occurred in a downstream direction, even though increasing temperatures, lower amounts of precipitation and higher rates of evapotranspiration at the south end of the Basin contribute to a change in biogeoclimatic zones (from Ponderosa Pine to Bunchgrass) at roughly Skaha Lake (BC MOE, September 2008). This was reasonable as all sampling stations, and thereby the Okanagan River system, were located (1) in the same valley bottom, (2) within an elevation of roughly 65m, and (3) within a distance of roughly 140km. During select sampling periods, the southern sampling stations exhibited more positive values, however, this observation was not consistent throughout the entire sampling program. At times, samples collected from the

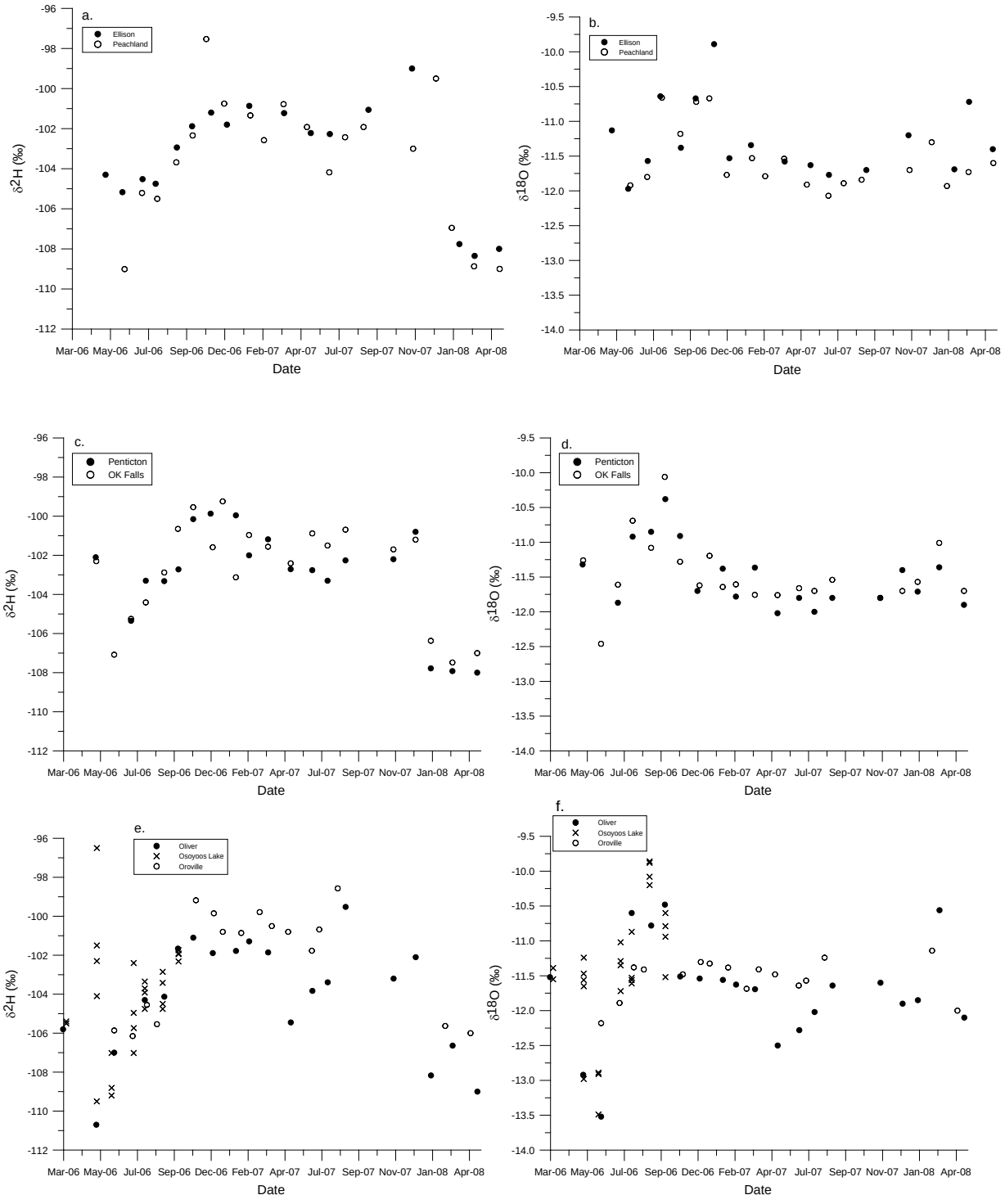

Figure 4.3. Seasonal pattern in δ^2H values (a.) and $\delta^{18}O$ values (b.) of surface water samples collected in Ellison and Peachland, BC, Canada; δ^2H values (c.) and $\delta^{18}O$ values (d.) of surface water samples collected in Penticton and OK Falls, BC, Canada; and δ^2H values (e.) and $\delta^{18}O$ values (f.) of surface water samples collected in Oliver and Osoyoos Lake, BCs, Canada and in Oroville in the United States.

north end of Okanagan Lake (Ellison) were slightly more positive than those collected in the central portion of Okanagan Lake (Peachland). The Ellison station was located within a small "arm" at the top of Okanagan Lake ("Vernon Arm"), and the slightly enriched values may reflect a lower degree of flow/water circulation in that arm of Okanagan lake. Variations in δ^2H and $\delta^{18}O$ values between sampling stations during each monthly sampling event were relatively small. The monthly variation in δ^2H values was up to 3‰, while the variation in $\delta^{18}O$ values was up to 1.5‰ (Figure 4.3).

The negligible spatial variations in δ^2H and $\delta^{18}O$ values of surface water samples suggests that the Okanagan River system behaves as a single hydrologic unit rather than as a series of independent lakes. The isotopic compositions of water bodies in the Okanagan River system downstream of Okanagan Lake, including Okanagan River, Skaha Lake and Vaseaux Lake (both of which were not sampled directly) and Osoyoos Lake, were similar to the isotopic composition of Okanagan Lake, suggesting that the major input of water into these downstream water bodies was Okanagan Lake.

4.4.1.3 Relationship With Precipitation

Precipitation in the Okanagan Basin is characterized by large seasonal variations in amount and isotopic composition, with minimum isotopic values occurring in the winter and maximum values occurring in the summer/early fall. Overall differences of 110‰ and 16.9‰ were measured for δ^2H values and $\delta^{18}O$ values in precipitation, respectively, from winter to summer. Despite the large seasonal variations in precipitation, the seasonal variation in δ^2H and $\delta^{18}O$ values of surface waters in the Okanagan River system was smaller, with a difference in δ^2H values of up to 13‰ and a difference in $\delta^{18}O$ values of up to 3.6‰.

4.4.1.4 Okanagan River System Dynamics

Okanagan Lake is a warm monomictic lake that stratifies in spring and mixes through the winter (Nordin, 2005). The more negative δ^2H and $\delta^{18}O$ values of surface waters observed in May and June likely correspond to recharge by snowmelt and spring rains. The trend towards more positive δ^2H and $\delta^{18}O$ values over the summer and early fall (in Okanagan Lake and south along the Okanagan River system) was indicative of evaporation. The δ^2H and $\delta^{18}O$ values peaked in September and October and then shifted towards more negative δ^2H and $\delta^{18}O$ values, likely indicative of fall turnover and mixing with deeper waters.

The main inflow into Okanagan Lake from watershed creeks and tributaries generally occurs in May and June in the form of snowmelt and spring rains (Nordin, 2005). The δ^2H and $\delta^{18}O$ values of surface water samples collected along the Okanagan River system between February 2006 and April 2008 were lower than δ^2H and $\delta^{18}O$ values of winter and spring precipitation of the Okanagan Basin, suggesting that evaporative processes had occurred. It has been reported that approximately 12% of precipitation reaches Okanagan Lake, with roughly 85% lost to evaporation and evapotranspiration and the remainder exiting the lake (Nordin, 2005). Thus δ^2H and $\delta^{18}O$ values of surface waters along the Okanagan River System may be indicative of evaporation of waters within watershed creeks and tributaries prior to entering Okanagan Lake, with additional evaporation of waters during storage within Okanagan Lake and the Okanagan River system. While isotopic enrichment of water occurs during evaporation, evapotranspiration does not result in isotopic partitioning of ^2H and ^{18}O (Clark and Fritz, 1997).

For Osoyoos Lake, δ^2H and $\delta^{18}O$ values of composites water samples were within the range of δ^2H and $\delta^{18}O$ values of waters collected near-surface. The δ^2H and $\delta^{18}O$ values of samples collected from two Town of Osoyoos pumphouses that draw water from the bottom of

Osoyoos Lake (-107 to -101‰ for δ^2H; -12.2 to -10.6‰ for $\delta^{18}O$) were also within the range of δ^2H and $\delta^{18}O$ values of waters collected near-surface. The δ^2H and $\delta^{18}O$ values of all water samples collected from Osoyoos indicated that the lake may be well mixed.

4.4.1.5 Relationship Between δ^2H and $\delta^{18}O$ Values

The δ^2H and $\delta^{18}O$ values of surface waters in the Okanagan River system are plotted on a δ^2H-$\delta^{18}O$ diagram along with the LMWL for West Kelowna (Figure 4.4). The LMWL for Osoyoos is shown for reference, however, as most of the water in the south portion of the Basin originates above the outlet of Okanagan Lake, it was necessary to compare the δ^2H and $\delta^{18}O$ values of surface waters to those of precipitation recharging Okanagan Lake in the northern

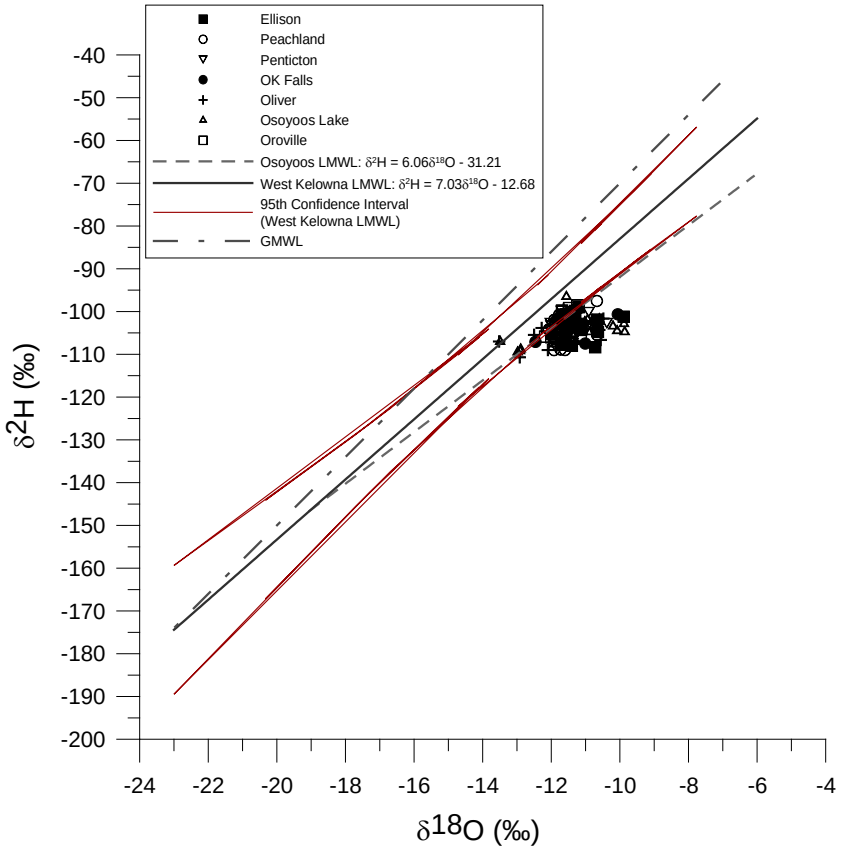

Figure 4.4. δ^2H-$\delta^{18}O$ diagram showing δ^2H and $\delta^{18}O$ values of surface samples collected along the Okanagan River system in British Columbia, Canada, between February 2006 and April 2008. The LMWL for West Kelowna (and the 95th confidence interval of the regression line for West Kelowna precipitation), the LMWL for Osoyoos and the GMWL (Craig, 1961) are shown.

portion of the Basin. The δ^2H and $\delta^{18}O$ values of surface waters plot in a tight cluster near the region of spring precipitation, and to the right of the LMWLs for Osoyoos and, in particular, West Kelowna.

Linear regression was completed for samples collected at each sampling station in an attempt to define an evaporation line for each station. The equations of the regression lines are provided in Table 4.3. It was evident that the linear relationship between the δ^2H and $\delta^{18}O$ values at each sampling station did not represent an evaporation line for that station. The lines for all equations intersected the Osoyoos LMWL and/or West Kelowna LMWL in the region of spring and summer precipitation, thereby, assuming that the initial isotope composition of water input by precipitation was that of spring/summer precipitation. This is not the case for the Okanagan Basin, as the Basin receives the majority of its recharge by snow-melt and spring rainfall events. Additionally, these linear regression equations all had slopes of less than 3.9, corresponding to a humidity of 0% (Gonfiantini, 1986). As the mean relative humidity (RH) for Kelowna and Penticton ranges between 52% (3pm land surface temperature [LST]) and 78% (6am LST) (EC, February 2008), and based on the relationship between isotopic enrichment in evaporating water and the effect of humidity, the LEL for the Okanagan River system is expected to have a theoretical slope of between 4.6 and 5.4 (Gonfiantini, 1986). These slope

Table 4.3. Summary of linear regression equations calculated for surface water samples collected along the Okanagan River system in British Columbia, Canada, between February 2006 and April 2008 (note, the four stations on Osoyoos Lake were combined).

Station	Station ID	Linear Regression Equations	R^2
Ellison	2	$\delta^2H = 0.28\ \delta^{18}O - 100.23$	0.00
Peachland	3	$\delta^2H = 2.40\ \delta^{18}O - 75.82$	0.11
Penticton	6	$\delta^2H = 1.18\ \delta^{18}O - 89.52$	0.04
OK Falls	7	$\delta^2H = 1.03\ \delta^{18}O - 90.96$	0.04
Oliver	13	$\delta^2H = 1.58\ \delta^{18}O - 85.59$	0.17
Oroville	109	$\delta^2H = 4.52\ \delta^{18}O - 50.20$	0.21
Osoyoos Lake	15, 33, 83, 107	$\delta^2H = 1.58\ \delta^{18}O - 86.25$	0.27

values of 4.6 and 5.4 have corresponding theoretical relative humidity values of 50 and 75%, respectively (Gonfiantini, 1986). The reason for the much shallower slopes was that the linear relationships did not account for the true initial isotope composition of water input by snow-melt and early spring precipitation.

4.4.1.6 Development of Local Evaporation Line for Okanagan River System

The δ^2H and $\delta^{18}O$ values of surface waters at a given location in a watershed are dependent on the initial isotopic composition of water input by precipitation and the subsequent effect of evaporation on water as it travels through a watershed (Ferguson et al., 2007). In general, δ^2H and $\delta^{18}O$ values from locations at or near headwater sites are depleted in heavy isotopes due to the influence of snowmelt, high-elevation rain, and/or glacial runoff, whereas δ^2H and $\delta^{18}O$ values further downstream are enriched in heavy isotopes as a result of evaporation (Ferguson et al., 2007; Froehlich et al., 2005). Surface waters are typically more enriched in ^2H and ^{18}O with respect to local precipitation and tributaries (Froehlich et al., 2005). However, increases in δ^2H and $\delta^{18}O$ values with downstream distance in a river basin can also be explained by mixing of tributary water and/or groundwater having higher δ^2H and $\delta^{18}O$ values than the river basin (Rock and Mayer, 2007). For this study, water samples at or near the headwater sites of the Okanagan River system were not obtained, however, they were inferred by highland groundwater samples collected from the south Okanagan Basin between April 2006 and September 2008. Based on the relatively narrow range of δ^2H and $\delta^{18}O$ values for sampling stations within Okanagan Lake (*i.e.*, Ellison and Peachland), input from groundwater and tributaries may be insignificant (or constant) relative to the contribution from precipitation at or near headwater sites.

Wolfe et al. (2007) define the theoretical LEL using three parameters: δ_P, the mean amount-weighted isotopic composition of precipitation; δ_{SSa}, the isotopic composition of waters in a closed basin in which evaporation equals inflow (E/I = 1) from precipitation δ_P under isotopic steady-state; and δ^*, the theoretical maximum (limiting) isotopic enrichment of water in a desiccating basin. The theoretical LEL is a straight line that extends from δ_P through δ_{SS} to δ^* and represents the isotopic evolution of water in a ***closed basin*** with inputs of mean amount-weighted precipitation (δ_P) evaporating towards δ^* (Wolfe et al., 2007). Deviations from this line occur as a result of differing amounts of seasonal precipitation and groundwater influx, which causes a decrease in the intercept of the LMWL and LEL from δ_P to $\delta_{groundwater}$, and an increase in the slope of the observed relationship between δ^2H and $\delta^{18}O$ relative to the theoretical LEL (Wolfe et al., 2007).

To develop the LEL for the Okanagan River system, the mean isotopic composition of sixty highland groundwater samples was used to represent the δ_P parameter. The δ_P value is effectively the initial isotopic composition of the water (input by precipitation) prior to evaporation. The δ_{SS} parameter was calculated as (1) the mean isotopic composition of 138 surface water samples collected from the Okanagan River system (δ_{SSa}), and (2) the mean isotopic composition of 10 other surface water samples, excluding those from Anarchist Mountain and Mt. Baldy where significant evaporation did not appear to have taken place (δ_{SSb}). The isotopic composition of the δ_P and δ_{SS} parameters are provided in Table 4.4.

Table 4.4. δ^2H and $\delta^{18}O$ values used for calculation of the LEL for the Okanagan River system in British Columbia, Canada.

Parameter	**δ^2H (‰)**	**$\delta^{18}O$ (‰)**
δ_P	-132	-16.8
δ_{SSa}	-103	-11.5
δ_{SSb}	-78	-6.0

The δ_P, δ_{SSa} and δ_{SSb} parameters are plotted on a δ^2H-$\delta^{18}O$ diagram (Figure 4.5). A straight line extending through δ_P and δ_{SSa} resulted in the equation $\delta^2H=5.41\delta^{18}O–41.15$ for the LEL of the Okanagan River system. The slope of the LEL (*i.e.*, 5.41) was close to the range of slopes predicted from mean relative humidity values for the Okanagan Basin (*i.e.*, 4.6 to 5.4). The slope of the LEL was lower than that of the LMWL for Osoyoos (*i.e.*, 6.06) and even lower than that of the LMWL for West Kelowna (*i.e.*, 7.03). The lower slope suggested that surface waters of the Okanagan River system had undergone evaporation within watershed creeks and

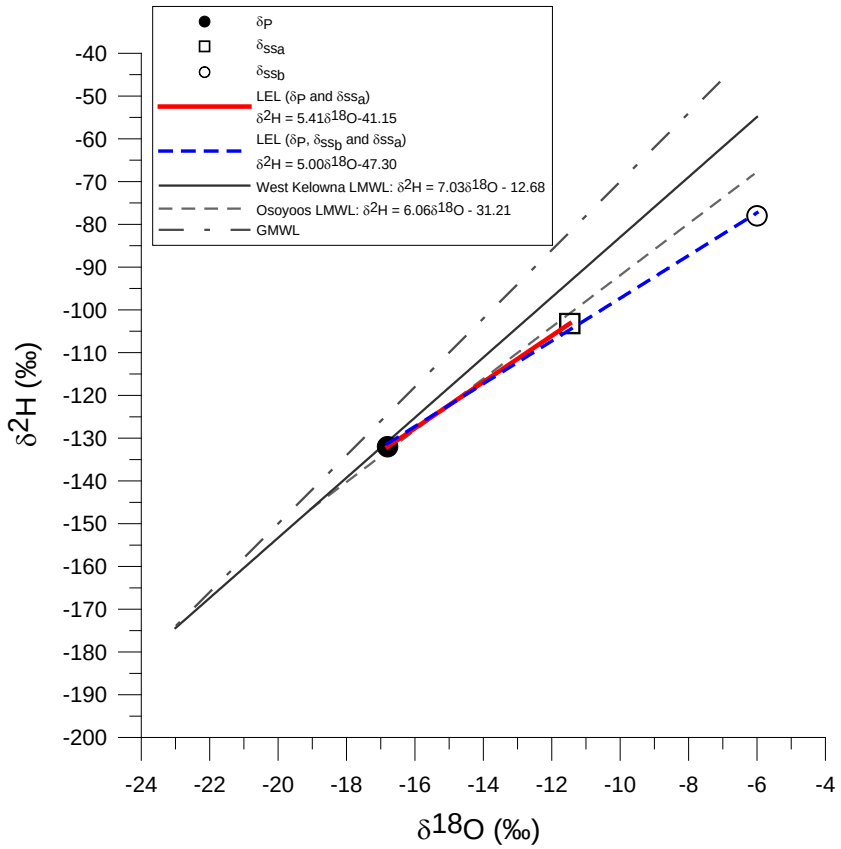

Figure 4.5. δ^2H-$\delta^{18}O$ diagram showing LELs for the Okanagan River system in British Columbia, Canada, calculated using the mean isotopic compositions of: highland groundwater samples (δ_P), surface water samples collected from the Okanagan River system (δ_{SSa}), and other surface water samples collected from the south Okanagan (δ_{SSb}). The LMWLs for West Kelowna and Osoyoos and the GMWL (Craig, 1961) are shown.

tributaries prior to entering Okanagan Lake and during storage within Okanagan Lake and the Okanagan River system. Incorporation of the δ_{SSb} parameter gives the equation $\delta^2H=5.00\delta^{18}O-47.30$, which also had a slope close to the predicted slope.

4.4.1.6.1 Calculation of E/I Ratio

The E/I ratio was calculated assuming that evaporation of surface waters within the Okanagan River system took place within watershed creeks and tributaries and during storage in the Okanagan River system. The E/I ratio was calculated in terms of ^{18}O using Equation 2.10 and parameters provided in Table 4.5, where t is temperature calculated using 2006 and 2007 data from Kelowna and 2005 and 2007 data from Osoyoos (EC, February 2008), h is humidity (estimated from Gonfiantini (1986) for the slope of the LEL for the Okanagan Basin [*i.e.*, 5.41]), δ_P the mean isotopic composition of highland groundwaters (or, in this case, of initial precipitation prior to evaporation), δ_A the isotopic composition of ambient atmospheric moisture (where $\delta_A = \delta_P - \varepsilon$), $\varepsilon^{18}O_{l\text{-}v}$ the equilibrium fractionation factor for water-vapour exchange based on a mean annual temperature of 9.7°C (Equation 2.5) α a fractionation factor ($\varepsilon = \alpha + 1$), $\Delta\varepsilon$ the kinetic fractionation factor for exchange between the boundary layer and laminar layer (Equation 2.6) and δ_L the isotopic composition of lake water ($\delta_L = \delta_{SSa}$). The E/I ratio was 0.31, indicating that the estimated fraction of water loss by evaporation in the Okanagan River system could be up to 31 ± 5%.

Table 4.5. Parameters used for calculation of the E/I ratio in terms of ^{18}O for the Okanagan Basin, British Columbia, Canada.

Input Parameters								
T (°C)	**T (K)**	**h (%)**	**δ_P (‰)**	**δ_A (‰)**	**$\varepsilon^{18}O_{l\text{-}v}$ (‰)**	**α**	**$\Delta\varepsilon^{18}O_{bl\text{-}v}$ (‰)**	**δ_L (‰)**
9.7	282.9	78	-16.8	-27.5	10.7	9.7	3.1	-11.5 ± 0.7

4.4.1.6.2 Calculation of Average Evaporative Loss

Average evaporative loss (*l*) was calculated using the same assumption: that evaporation of surface waters took place within watershed creeks and tributaries and during storage within the Okanagan River system. The average evaporative loss was also calculated in terms of ^{18}O for the Okanagan River system based on the linear relationship between annual average δ^2H and $\delta^{18}O$ values, as in Clark and Fritz (1997) and Rock and Mayer (2007). Average evaporative loss was calculated using the parameters provided in Table 4.6 and the following equations:

$$\Delta^{18}O_{v\text{-}w} = \varepsilon^* * \ln(f) \quad (4.1)$$

$$l = 100[1\text{-}\exp(f)] \quad (4.2)$$

where $\Delta^{18}O_{v\text{-}l}$ is the average annual evaporative enrichment of vapour relative to water, ε^* is calculated using Equation 2.8, and *f* the residual water fraction. $\Delta^{18}O_{v\text{-}l}$ is the difference between $\delta^{18}O_{vapour}$ and $\delta^{18}O_{water}$, or in this case between $\delta^{18}O_{SSa}$ and $\delta^{18}O_P$. For ε^*, $\varepsilon^{18}O_{v\text{-}l}$ is the equilibrium fractionation factor for vapour-water exchange based on a mean annual temperature of 9.7°C (Equation 2.5); and $\Delta\varepsilon^{18}O_{v\text{-}bl}$ the kinetic enrichment factor for vapour-water exchange and is based on a slope of 5.41 and a corresponding relative humidity (h) of 78% (Gonfiantini, 1986).

Table 4.6. Parameters used for calculation of the average evaporative loss in terms of ^{18}O for the Okanagan River system in British Columbia, Canada.

Input Parameters							
δ_P (‰)	**δ_{SSa} (‰)**	**$\Delta^{18}O_{v\text{-}w}$ (‰)**	**$\varepsilon^{18}O_{v\text{-}l}$ (‰)**	**$\Delta\varepsilon^{18}O_{v\text{-}bl}$ (‰)**	**ε^* (‰)**	**ln (*f*)**	***f***
-16.8	-11.5 ± 0.7	5.3	-10.7	-3.1	-13.8	-0.38	0.68

The residual water fraction for the Okanagan River system was approximately 68%, resulting in an average evaporative loss of up to 32 ± 6%. This is similar to that calculated using the E/I equation.

Potential error in the calculations for E/I and average evaporative loss may be due to: (1) uncertainty in the relative amount of evaporation of surface waters taking place within watershed creeks and tributaries prior to entering Okanagan Lake; (2) the humidity value (78%) was taken from Gonfiantini (1986) and was based strictly on the slope of the LEL for the Okanagan Basin. The humidity value is within the range of humidity values for the Okanagan Basin (52 to 78%); however, it may not be representative of the less humid conditions in the summer/early fall when isotopic enrichment takes place; (3) the temperature used in the calculations (9.7°C) is the approximate mean annual temperature for the Okanagan Basin, and may not be representative of the warmer conditions that occur when isotopic enrichment takes place; (4) the initial isotopic composition of the headwaters is inferred to be that of highland groundwaters; and (5) none of the parameters were evaporation-flux weighted, again, not accurately representing the conditions in the summer/early fall when isotopic enrichment is greatest. Note that E/I and average evaporative loss reflect water that is lost to evaporation, and not to evapotranspiration.

4.4.2 Other Surface Water Bodies

4.4.2.1 δ^2H and $\delta^{18}O$ Values

The δ^2H and $\delta^{18}O$ values of surface water samples collected from the other surface water bodies in the south Okanagan Basin between April 2006 and September 2008 are presented in Table B-1 of Appendix B and plotted on a δ^2H-$\delta^{18}O$ diagram (Figure 4.6). The δ^2H and $\delta^{18}O$ values of surface waters within the valley bottom ranged from -101 to -85‰ (mean of -92 ± 8‰) and -10.7 to -4.7‰ (mean of -8.5‰ ± 2.4‰), respectively. With the exception of two samples collected from the kettle lake (samples 2 and 3) on July 27th and September 30th, the positive δ^2H and $\delta^{18}O$ values indicated that evaporation of the surface water bodies had occurred.

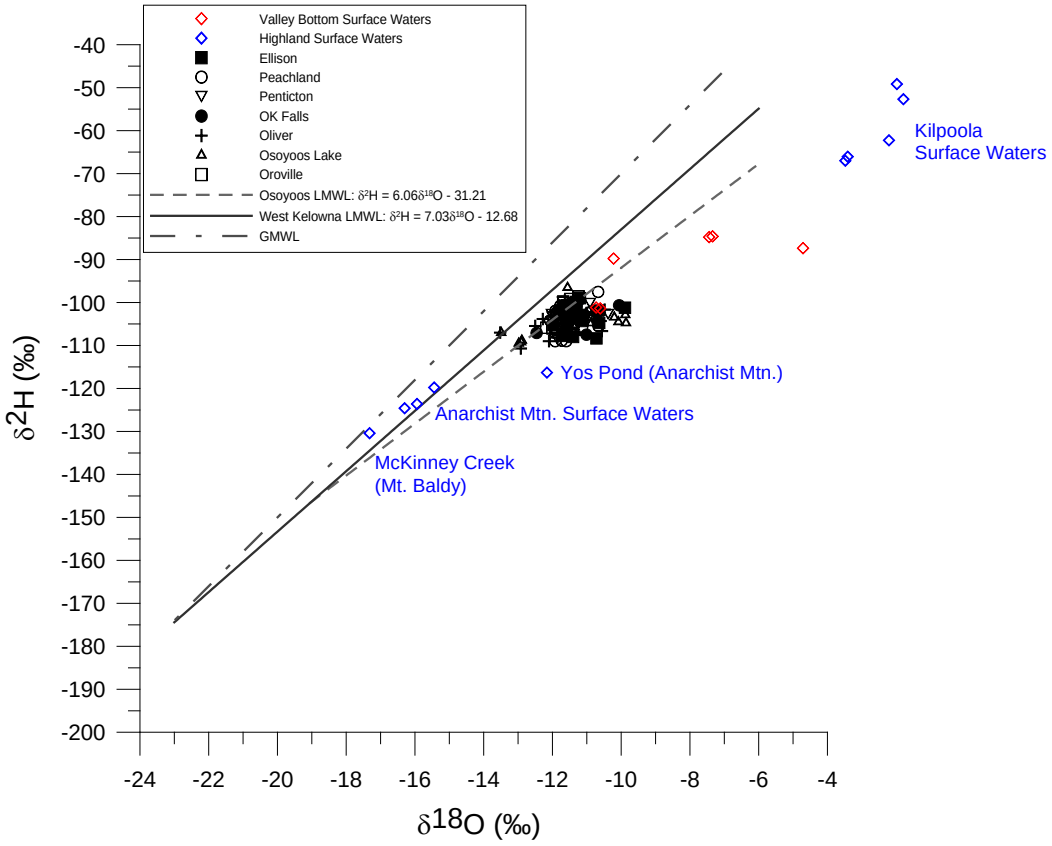

Figure 4.6. δ^2H-$\delta^{18}O$ diagram showing δ^2H and $\delta^{18}O$ values of 15 other surface water samples collected in the South Okanagan Basin, British Columbia, Canada, between May 2006 and September 2008. LMWLs for West Kelowna and Osoyoos and the GMWL (Craig, 1961) are shown.

Samples 2 and 3 from the kettle lake both had δ^2H values of -101‰, and $\delta^{18}O$ values of -10.7‰ and -10.6‰, respectively. These values were similar to those from the lakes and river of the Okanagan River system. As the land around this lake received irrigation water from Osoyoos Lake, these values likely represent irrigation return flow that had undergone no, to slight, subsequent evaporation. The δ^2H and $\delta^{18}O$ values of surface waters on Kilpoola Mountain ranged from -66 to -49‰ (mean of -56 ± 9‰) and -3.4 to -1.8‰ (mean of -2.4‰ ± 0.9‰), respectively. The positive δ^2H and $\delta^{18}O$ values indicated that evaporation of the surface water bodies had occurred. The δ^2H and $\delta^{18}O$ values of surface waters at Taylor, Chapman and Haynes Creek ranged from -125 to -120‰ (mean of -123 ± 3‰) and -16.3 to -15.4‰ (mean of

-15.9‰ ± 0.4‰), respectively. The δ^2H and $\delta^{18}O$ values at Yos Pond were -116 and -12.2‰, respectively. Those at McKinney Creek were -130 and -17.3‰, respectively. The more negative values of Anarchist Mountain and Mt. Baldy were indicative of surface waters recharged by precipitation and/or groundwater with no significant evaporation (Taylor, Chapman and Haynes Creek, and McKinney Creek) to potentially some evaporation (Yos Pond) occurring.

4.5 Summary and Conclusions

The Okanagan River system appears to behave as a single hydrologic unit. Okanagan Lake, the largest of the four lakes within the main trench of the Okanagan Basin, is located at the top of the Okanagan River system and receives the majority of its input via precipitation at or near its headwaters in the winter/early spring. Water originating above the outlet of Okanagan Lake discharges into the Okanagan River and Skaha, Vaseaux and Osoyoos lakes, and is the source of water exiting the Okanagan Basin. Water from the outlet of Okanagan Lake is discharged south into the Okanagan River system to Oroville, United States over a period of roughly two years, based on the residence times of water in Skaha, Vaseaux and Osoyoos Lakes. The isotopic compositions of water bodies in the Okanagan River system downstream of Okanagan Lake are similar to the isotopic composition of Okanagan Lake, suggesting that the major input of water into these downstream water bodies is Okanagan Lake.

The δ^2H and $\delta^{18}O$ values of surface waters were more positive than those of precipitation in the Okanagan Basin, indicative of evaporation of surface waters. The more negative δ^2H and $\delta^{18}O$ values of surface water samples of Okanagan Lake occurred in the spring months of May and June, and were indicative of recharge by snowmelt and spring rains. Some degree of evaporation of surface waters of the Okanagan River system and its tributaries during the summer and early fall resulted in a trend towards more positive δ^2H and $\delta^{18}O$ values. During

fall turnover of Okanagan Lake, the shift towards negative δ^2H and $\delta^{18}O$ values was indicative of shallow waters mixing with deeper waters. Insufficient data was available to confirm the degree of evaporation from watershed creeks and tributaries prior to waters entering Okanagan Lake relative to the degree of evaporation during storage within Okanagan Lake and the Okanagan River system. Assuming a closed basin, up to 32% of water was lost to evaporation. Using the mean isotopic composition of highland groundwaters (inferred to represent precipitation at or near the headwaters) and the mean isotopic composition of the surface water samples collected in the Okanagan River system, the equation of the LEL for the Okanagan River system is $\delta^2H = 5.41\delta^{18}O–41.15$. The slope is close to that predicted from mean relative humidity values for the Okanagan Basin (*i.e.*, 4.6 to 5.4). The slope of the LEL is lower than that of the LMWL for West Kelowna (slope of 7.03) indicating that the surface waters of the Okanagan River system had undergone evaporation.

Note that these are preliminary conclusions as there is insufficient data to accurately comment on the dynamics of Okanagan Lake and the Okanagan River system. To better understand the characteristics of Okanagan Lake and other lakes of the Okanagan River system (including mixing, residence and recharge source[s]), all surface water and groundwater inputs and outputs would need to be quantified.

4.6 Acknowledgements

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outings in 2006 to collect water samples from Osoyoos Lake. Thanks to Jim Hendry and Teresa Salamone for collecting samples at the Oroville station. Thanks to Len Wassenaar, Geoff Kohler and Virginia Chostner for analyzing samples.

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CHAPTER 5
REGIONAL HYDROGEOLOGY OF THE SOUTH OKANAGAN BASIN, BRITISH COLUMBIA, CANADA

Abstract. Sustainability of surface water and groundwater resources is a key issue in the Okanagan Basin, British Columbia, Canada. Osoyoos, located in the South Okanagan valley, is the warmest and driest region in the Basin and is dependent on limited surface water and groundwater resources for irrigation and domestic needs. Best management of these resources requires an understanding of the hydrogeological setting of the region, including the source(s) of recharge of its water systems. The purpose of this study was to characterize the regional hydrogeological setting of the south Okanagan Basin, specifically the area west of Osoyoos Lake, and to quantify recharge sources to shallow and deep groundwater systems. Groundwater samples were collected from 82 wells, 5 municipal water supplies and 3 springs between February 2006 and April 2008 and analysed for stable isotopes of water (^{2}H and ^{18}O), age dates (radiocarbon [^{14}C], enriched tritium [^{3}H] and tritium-helium [$^{3}H/^{3}He$]), and/or major and trace groundwater chemistry. Additionally, groundwater levels were monitored in 31 wells. Recharge of groundwater in bedrock of highland areas east and west of Osoyoos was via snow-melt and spring rains. West of Osoyoos Lake, highland areas were not the dominant source of recharge for shallow or deep confined groundwaters in the benchlands and valley bottom. Recharge of shallow groundwaters in non-irrigated benchlands of West Osoyoos was from annual precipitation, while recharge of shallow groundwaters in irrigated benchlands and valley bottom of West Osoyoos was predominantly via irrigation water derived from Osoyoos Lake. In irrigated areas of West Osoyoos, high concentrations of nitrate in shallow groundwaters indicated that these groundwaters were highly susceptible to anthropogenic contamination. Precipitation falling in the highlands likely recharges deeper, or basal, deposits of the South Okanagan Basin valley. Recharge of deep confined groundwater occurred up to one thousand years ago, however, the source of recharge was not confirmed.

Key Words: regional hydrogeology, semi-arid, recharge, isotopes, age dating, groundwater chemistry, irrigation.

5.1 Introduction

The sustainability of an adequate supply of surface water and groundwater is a key issue in the Okanagan Basin, located in the Southern Interior Plateau of British Columbia, Canada. A rapidly growing population, increase in land development, and changes in land-use are expected to place additional stresses (*i.e.*, increase in human consumption, irrigation) on surface water and groundwater resources in this semi-arid region (Cohen et al., 2006). Because the Okanagan Basin receives little precipitation during the winter and spring owing to its location in the rain shadow of the Coast and Cascade Mountains, management and conservation of these water resources are especially critical (Cohen and Kulkarni, 2001; Merritt et al., 2006; Neilsen et al., 2001). An up-to-date water supply and demand study of the entire Okanagan Basin (within Canada) is currently being completed by the Okanagan Basin Water Board and the Province of BC, and basin-wide interest in the sustainability of water resources is evident by the numerous articles published in local newspapers and popular media (Casey, 2008).

A recent 'State-of-the-Basin' report published for the Okanagan Basin Water Board as part of the Water Supply and Demand Project identifies the need for developing an understanding of regional-scale hydrogeologic processes in the Okanagan Basin (Neilson-Welch and Allen, 2007), and supports the concept that management of surface water and/or groundwater resources requires knowledge of the hydrogeological setting, including an understanding of the recharge source(s) to the water system. As part of identifying the recharge source(s), knowledge of the age and movement of groundwater has significant implications for assessment of vulnerability (Bouhlassa and Aiachi, 2002). The use of old groundwater (or, groundwater that is not actively recharged) is essentially a non-renewable process, termed "*mining*" (Bouhlassa and Aiachi, 2002). Shallow groundwater is, generally, continuously

renewed, and thus potentially sustainable (Bouhlassa and Aiachi, 2002), however, shallow groundwater can be more susceptible to anthropogenic contamination.

Osoyoos and the surrounding rural area (study area) is the driest and warmest region of the Okanagan Basin. Residential, agricultural and viticultural developments extend from the valley bottom adjacent to Osoyoos Lake up into the benchlands. Residential developments reach into the highlands of Kilpoola Mountain to the west, Anarchist Mountain to the east and Mt. Baldy to the northeast (Figure 5.1). With agriculture as its main industry, the economic sustainability of the Osoyoos area is critically dependent on an adequate supply of irrigation water from Osoyoos Lake (Neilsen et al., 2001). Osoyoos Lake is primarily fed by the Okanagan River system and, in turn, recharged by snow-melt from mountain catchments as runoff or via groundwater recharge. Thus, a decrease in the availability of water in catchment areas during the peak growing season (as a result of a reduced snow-pack and early snow-melt), coupled with an increase in crop water demand, would result in limited availability of irrigation water.

The Osoyoos area relies heavily upon its groundwater resources, as evidenced by the substantial number of provincially-registered groundwater wells (in excess of 250). In the valley bottom and benchlands, groundwater is predominantly recharged by irrigation water obtained from Osoyoos Lake, as identified in this study and by Piteau Associates (1989). A decrease in the availability of irrigation water would result in lower recharge to groundwater aquifers and, thus, lower yields to existing groundwater wells. In the mountainous highlands, residential developments are solely dependent on groundwater for their consumptive and irrigation needs, and reduced availability of groundwater (*i.e.*, from a reduced snow-pack and/or increase in water use) would result in less water available in the highland aquifers.

Figure 5.1. View (looking north) of Osoyoos, British Columbia, Canada. Kilpoola Mountain is to the left of the photo and Anarchist Mountain is to the right of the photo.

Despite the region's dependence on surface water (Okanagan River system) and groundwater resources, and given the potential fate of these resources to increased demand, detailed regional hydrogeological studies have not been completed for the Osoyoos area. Regional scale investigations have been conducted for groundwater quality with respect to nutrient and pesticide loadings (Hodge, 1985; Hodge, 1986; Piteau Associates, 1989; York, 1994). An understanding of the interaction between the key groundwater systems in the highlands, benchlands and valley bottom of the Osoyoos area, and their respective recharge sources, as well as an understanding of the interaction between surface water and groundwater systems, is essential in developing strategies to ensure sustainability of the region's water supplies.

Stable isotopes of water, coupled with radiometric age dating and geochemical and/or physical parameters, have been successfully used in previous studies to identify recharge sources and residence times (Clark et al., 1998; Douglas et al., 2007; Palmer et al., 2007; Tsujimura et al., 2007), to understand flow paths and mixing between flow systems (Clark et al., 1998; Plummer et al., 2004), and to asses surface water and groundwater interactions (Harvey et al., 2006). The objectives of this study were to characterize the regional hydrogeological setting of

the south Okanagan Basin, specifically the Osoyoos area west of Osoyoos Lake, and to quantify recharge sources to shallow and deep groundwater systems within the study area. To achieve this, a two-year study was completed, where stable isotopes of water ($\delta^{2}H$ and $\delta^{18}O$), coupled with radiocarbon (^{14}C), enriched tritium (^{3}H) and/or tritium/helium ($^{3}H/^{3}He$) age dating, geochemical analyses (major and trace groundwater chemistry) and physical parameters (water levels), were used to evaluate the hydrogeological setting and recharge sources for the region. This study is intended to be used as groundwork for future supply and demand studies in the south Okanagan Basin and as a model for future studies in other areas of the interior of British Columbia where stable isotopes of water, coupled with age dating, geochemical and physical parameters, are applied to evaluate recharge sources.

5.2 Study Area

The Town of Osoyoos and rural areas straddle the east and west sides of Osoyoos Lake, a trans-boundary lake shared with the United States. Osoyoos Lake is located within the Okanagan River valley at an elevation of approximately 278 metres above sea level (masl). On the west side of Osoyoos Lake, the land surface rises in a series of 200 to 400 m wide benches (benchlands). Each bench rises up roughly 20 m in elevation, to an approximate elevation of 350 masl at the upper-most bench. The upper-most bench rises steeply and contacts bedrock at an approximate elevation of 450 masl in the north portion of the study area and 400 masl in the south portion of the study area.

5.2.1 Climate

The Osoyoos area received an average annual total precipitation of 318 mm, with the greatest amount falling as rain between May and June , based on climate normals for the period between 1991 and 2000 (Environment Canada [EC], September 2008a). Between 2000 and

2007, the Osoyoos area received an estimated average annual total precipitation of 274 mm (EC, September 2008b). Average annual temperatures were 10.1°C, based on climate normals between 1991 and 2000 (EC, September 2008a) and evapotranspiration (ET) rates reached an average of 6.6 mm/day in July (Farmwest, 2008). For a majority of the year, ET generally exceeds precipitation, leading to moisture deficits of up to about 0.5 m (EC, September 2008b).

5.2.2 Geological Setting

The valley bottom and benchlands are comprised of glacial materials deposited 10,000 to 12,000 years ago during stages of retreat of the last advance of the Wisconsin (Fraser) glacial ice sheet, and of post-glacial materials deposited by alluvial fans, beaches and spits (Nasmith, 1962). Within the valley bottom, Osoyoos Lake occupies a depression formed by the melting of an extensive ice lobe segment (Nasmith, 1962). The benchlands are comprised of sand and gravel outwash terrace and kettled outwash (glaciofluvial) deposits that range from roughly 1 to 16 m in thickness (BC Ministry of Environment [BC MOE], September 2008; Nasmith, 1962; Piteau Associates, 1989). On individual benches, the ground surface is undulating, and within the central and south portions of the study area, kettle lakes (and remnants of kettle lakes - now filled in) are present. Glaciolacustrine and/or till deposits comprised of silt with varying amounts of clay, sand and gravel, underlie the glaciofluvial deposits (Nasmith, 1962; Piteau Associates, 1989). The silts have been classified as (1) glaciolacustrine in origin, deposited within glacial Lake Oliver which formed after ponds along the ice margins coalesced over the ice lobe that occupied the valley (Nasmith, 1962); and (2) as glacial till, based on their often gravelly nature and on the observation that kettle lakes on the ground surface appear to correspond to depressions in the surface of the silt (Piteau Associates, 1989). The surface of the silt deposits is undulating, likely a result of melting of stagnant masses of ice buried within the silts (Nasmith,

1962). In the north portion of the study area, the thickness of the silts is roughly 51 m in the upper bench (Knight, August 2008; BC MOE, September 2008) to 44 m near Osoyoos Lake (Paley, June 2006). In the central portion of the study area, the thickness is up to approximately 113 m (BC MOE, September 2008), and in the south, the thickness is greater than 19 m (Piteau Associates, 1989). The silt deposits transition from brown to grey at depths of greater than 16 m below the top of the silt (BC MOE, September 2008), corresponding to the reduction-oxidation boundary.

A >1.5 m thick layer of coarse gravel and cobbles is present below the glaciolacustrine and/or till deposits in the north portion of Osoyoos, west of Osoyoos Lake (Paley, June 2006). Little information is available for this unit. However, it is known that adjacent to Osoyoos Lake, it is present at a depth of roughly 47 m below ground surface (mbgs) and is overlain by approximately 3 m of coarse gravel near the ground surface followed by approximately 44 m of silt and clay. In the upper benchlands, the unit is thin (thickness unknown) and is overlain by approximately 51 m of silt and/or clay (Knight, August 2008). The extents of the coarse gravel and cobble layer to the north and south are not currently known.

5.2.3 Hydrogeological Setting

Shallow unconfined groundwater is present at the base of the glaciofluvial deposits. Where the surface of the glaciolacustrine and/or till unit is low (*i.e.*, in localized depressions), the thickness of the saturated glaciofluvial deposits is greater than where the surface of the glaciolacustrine and/or till deposits is high (Piteau Associates, 1989). Piteau Associates (1989) found that during the winter months, when groundwater levels were at their lowest, groundwater was contained in depressions in the surface of the sandy silt unit. According to BC MOE, an unconfined aquifer (Aquifer 193) encompasses the valley bottom and benchlands west of

Osoyoos Lake (BC MOE, September 2008). Aquifer 193 is roughly 25 km^2 in size and classified by the BC MOE as IIA: moderate demand, moderate productivity, and high vulnerability to contamination from surface sources (BC MOE, September 2008). Based on the terraced topography of the study area and the undulating nature of the surface of the glaciolacustrine and/or till unit, Aquifer 193 is inferred to be discontinuous. Irrigation water is the dominant source of recharge to the shallow unconfined aquifer (Piteau Associates, 1989). Deep confined groundwater is present in the coarse gravel and cobbles beneath the glaciolacustrine and/or till deposits.

Mountainous bedrock (highlands) is located on either side of the benchlands to elevations of up to 900 masl on Kilpoola Mountain and 1,900 masl on Mt. Baldy. The highlands are mostly comprised of granitic intrusive rocks (porphyritic granite, granodiorite, monzonite) of the Middle Jurassic and/or Middle Cretaceous periods, and metamorphic rocks (chlorite schist, greenstone, chert, minor ultramafic) of the Carboniferous to Permian period (Geological Survey of Canada, September 2008). One bedrock aquifer (Aquifer 248) is located in the developed portion of the highlands to the west (Kilpoola Mountain). Aquifer 248 is roughly 1 km^2 in size and is classified as IIIC: low demand, low productivity, and low vulnerability to contamination from surface sources (BC MOE, September 2008). Two bedrock aquifers (Aquifers 808 and 810) are located in the highlands to the east on Anarchist Mountain. Bedrock aquifers were not identified further east or northeast in the Bridesville and Mt. Baldy areas, respectively. Aquifer 808 is roughly 9.8 km^2 in size and classified as IIB: moderate demand, moderate productivity, and moderate vulnerability to contamination from surface sources, and Aquifer 810 is roughly 2.6 km^2 in size and classified as IIC: low demand, low productivity, and low vulnerability to contamination from surface sources (BC MOE, September

2008). Within the valley bottom and benchlands, bedrock is known to be present at a depth of about 51 mbgs in the north portion of the study area (Knight, August 2008) to 123 mbgs in the central portion of the study area (granitic bedrock) (BC MOE, September 2008). A schematic cross-section of the Osoyoos area is presented on Figure 5.2.

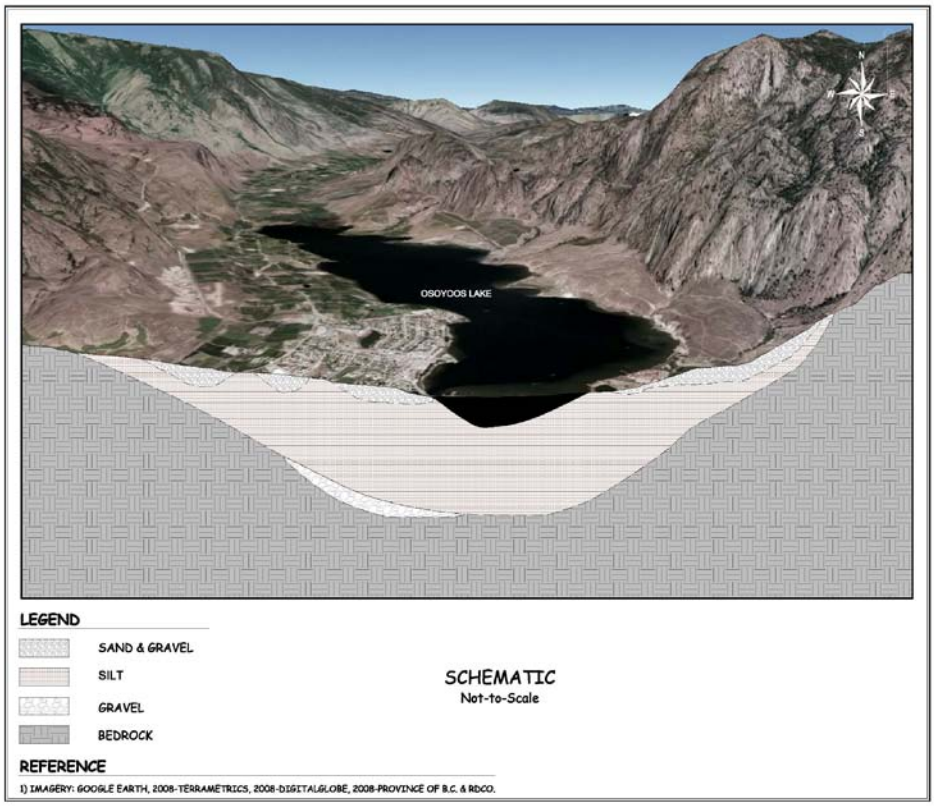

Figure 5.2. Schematic cross-section of the Osoyoos area, British Columbia, Canada.

5.3 Materials and Methods

Twenty-eight wells located within the valley bottom and benchlands of the study area were made available for sampling during the course of the research. Twenty of the wells (26, 28, 30, 35, 39, 42, 43, 44, 54a, 54b, 61, 62a, 62b, 66a, 66b, 70, 72a, 72b, 74a and 74b) are observation wells used for general monitoring purposes by BC MOE and EC. Eight of the wells (24, 25, 32, 37, 38, 46, 52 and 57) are domestic wells. To augment the existing monitoring well network, particularly in an area where subsurface drainage systems exist, nine research wells

(27a, 27b, 27c, 29a, 29b, 31a, 31b, 34a and 34b) were installed by the University of Saskatchewan Geology Department (USGD). In the highlands, eleven domestic wells located to the west on Kilpoola Mountain (16, 17, 18, 19, 20, 22, 23, 40, 41, 48 and 50) and 38 domestic wells located to the east on Anarchist Mountain (58-60, 64, 65, 68, 73, 76-80, 84-87, 89-98, 100-104, 106 and 108), at Bridesville (45, 53, 56 and 71) and on Mt. Baldy (11), were made available by their respective owners for sampling during the course of the research. Two municipal supply wells (9 and 10) located north of the study area in Oliver were also made available for sampling during the course of the research. Access to two Town of Osoyoos pumphouses (47 and 88), as well as an irrigation tap (36) from a user in the north portion of the study area serviced by 88, were provided for collection of irrigation water samples. Two springs on Anarchist Mountain (81 and 82) and one spring on Mt. Baldy (12) were also sampled. Groundwater well, pumphouse and spring locations and the location of the sampled irrigation tap are shown on Figure 5.3.

In the Osoyoos area, irrigation generally commences in mid-April and continues until mid-October. In 2006, irrigation began on April 1 (Doucette and Thomas, May 2006) and in 2007, irrigation began on April 15 (Doucette and Thomas, September 2008). Irrigation water for the study area is supplied by two pumphouses (47 and 88). The north portion of the study area receives water from pumphouse 88, which draws water from Osoyoos Lake via an intake located roughly 85 m out into the lake. The south portion of the study area receives water from pumphouse 47, which draws water from Osoyoos Lake via an intake located roughly 75 m out into the lake. Water is chlorinated at both pumphouses, and aerated at pumphouse 47, prior to its distribution for both domestic and irrigation purposes (Doucette and Thomas, May 2006). From the end of the irrigation season to the start of the next, water from the pumphouses is directed

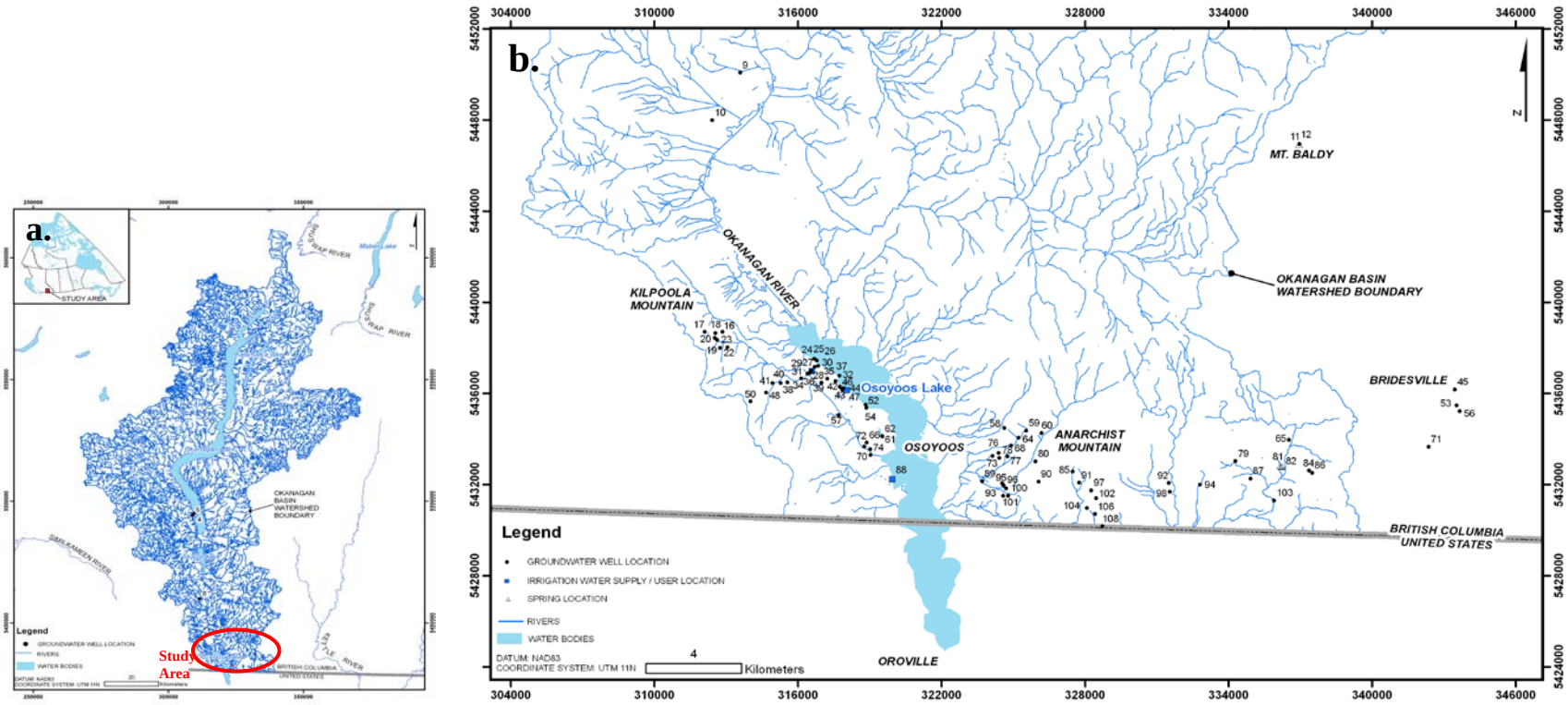

Figure 5.3. a. Location of study area within British Columbia, Canada and within the Okanagan Basin. Three groundwater wells (4, 5, and 8) located outside of the study area and sampled by others in 2004 are shown. b. Close-up of study area showing groundwater, irrigation water supply and spring sampling locations. Maps produced using river data from www.geobase.ca (National Hydro Network, station 08nm001) and national boundary line and water body data from DMTI Spatial Inc.

into a reservoir prior to distribution. However, when the demand for irrigation water increases at the start of the irrigation season, water is directly distributed to the orchards/vineyards. Two Town of Osoyoos wells (which were not used in this study) also provide water for early-season irrigation (Doucette and Thomas, May 2006).

An Agricultural Metering Pilot Program carried out by the Town of Osoyoos between April and October of 2006 at four orchards and two vineyards showed that irrigation rates at orchards ranged from approximately 1,400 to 2,700 m^3/hectare (ha) (average of 2,040 m^3/ha), while rates at vineyards were approximately 260 m^3 to 900 m^3/ha (average of 580 m^3/ha), or roughly 1/3rd of the irrigation rates at orchards (Doucette, September 2008).

5.3.1 Well Completion Details

Five USGD research boreholes were drilled along an east-west transect in the north portion of the study area between December 12 and 14, 2005 using a hollow stem auger rig. Two nested wells, one shallow and one deep, were installed in four of the five boreholes (wells 27b and 27c, 29a, 29b, 31a, 31b, 34a and 34b); a single well was installed in the remaining borehole (well 27a). The locations of the USGD research wells are shown on Figure 5.3. Shortly after installation, well 27b was damaged and was consequently not used in this study. Wells were constructed of 25 mm diameter, flush-threaded, Schedule 40 PVC casing with a 1.5 m long, 10-slot PVC screen. A filter pack consisting of clean silica sand was placed from 0.15 m to 0.3 m beneath the slotted well screen bottom to 0.15 to 0.3 m above the slotted well screen. A 0.9 m thick layer of bentonite chips, or bentonite pellets below the water table, was then placed as a seal above the filter pack. For the nested wells, in order to prevent the downward migration of groundwater from the shallow well to the deep well, a 0.9 m thick layer of bentonite pellets was also placed beneath the filter pack of the shallow well. Clean silica filter

sand was used to fill the remaining annulus up to a depth of roughly 1.5 mbgs. A surface seal, consisting of a 0.6 to 0.9 m thick layer of bentonite chips, was placed above the filter sand. Each well location was completed with a protective stand-up steel casing cemented in place.

Observation wells 26, 28, 30, 35, 39, 72a and 72b were completed by BC MOE between August 20 and September 5, 1969 using a rotary rig. The wells were completed with a 50 mm diameter, 1.5 m long, PVC screen, with filter sand placed around each well screen (Johanson, March 2006). It is not known what fill materials were used to fill the remaining annulus. Wells were completed with a protective stand-up steel casing cemented in place. Observations wells 42, 43, 44, 54a, 54b, 61, 62a, 62b, 66a, 66b, 70, 74a and 74b were completed by EC, as described in Piteau Associates (1989). For domestic and municipal wells, well completion depths and screened materials were obtained from the BC Water Resources Atlas (BC MOE, September 2008), where available, or from the individual well owner. Well completion depths, screen intervals and screened material(s) for each well (where known) are summarized in Table C.1 of Appendix C.

Of the 87 wells located within the study area, 25 wells were screened in the sands and gravels of Aquifer 193, 10 wells were completed in the top of the glaciolacustrine and/or till unit, one well was screened in the cobbles and gravel of the deep confined aquifer, one well was screened in overburden in the upper benchland, and 48 wells were set in bedrock of Aquifers 248, 808 and 810 or in bedrock with no identified aquifers. A water-bearing unit was present along the west edge of the study area, near the contact of the upper benchland and the bedrock. Only one well (38) is known to be completed in this unit. At this time, it is not known whether this unit forms part of Aquifer 193 or whether it is an isolated unit. The elevation of the wellhead of well 38 is roughly 100 m higher than wells in the valley bottom, and approximately

200 m lower than wells in the highlands of Kilpoola Mountain. This paper classifies well 38 and the associated water-bearing unit as being located in the "upper" benchland. The two Town of Oliver supply wells were completed in Aquifer 256, an unconfined sand and gravel aquifer.

5.3.2 Water Level Measurements

Within the valley bottom and benchlands, water levels were manually measured at all 20 observation wells, six domestic wells (25, 32, 52, 57, 37 and 33) and five research wells (27a, 27c, 29a, 29b and 31b) with an electronic water level probe on seven occasions between February and September 2006, and in February 2007. Water levels were not measured from research wells 31a, 34a and 34b, as these wells were dry during all monitoring events. Water levels were not measured at well 38 in the upper benchland, nor at any of the highland domestic wells, due to inaccessibility of the wellheads.

Continuous water levels were recorded at three observation wells (28, 30 and 35) and four research wells (27a, 27c, 29a and 31b) between June 2006 and August 2007 using Solinst Levelogger® Gold dataloggers programmed to record water levels at 15 minute intervals. The water levels were then corrected for barometric pressure using a Solinst Barologger® that had been set up in well 30 to take continuous measurements of barometric pressure. Water level data for the domestic well located in the deep confined aquifer was obtained from the well owner.

5.3.3 Water Sampling

Within the valley bottom and benchlands, groundwater samples were collected from all 20 observation wells, all eight domestic wells, five research wells (27a, 27c, 29a, 29b and 31b) and municipal (Oliver) supply wells 9 and 10. Irrigation water samples were collected from two pumphouses (47 and 88) and from the irrigation user (36). In order to better manage the large amount of data collected from shallow groundwater wells in the valley bottom and benchlands of

the Osoyoos area, wells have been grouped into North (wells 25, 26, 27a, 27c, 28, 29a, 29b, 30, 31b, 32, 35, 37 and 39), Central (wells 42, 43, 44, 46, 52, 54a, 54b and 57) and South (wells 61, 62a, 62b, 66a, 66b, 70, 72a, 72b, 74a and 74b). In the highlands, groundwater samples were collected from all 10 domestic wells on Kilpoola Mountain, all 33 domestic wells on Anarchist Mountain, all four domestic wells at Bridesville and the single well on Mt. Baldy. Water samples from natural springs were collected from the two springs on Anarchist Mountain and from the single spring on Mt. Baldy.

Prior to sample collection, all observation and research wells were purged until a minimum of three well volumes of groundwater had been removed (or until the wells went dry) and field parameter measurements (pH, temperature and/or dissolved oxygen) had stabilized. This ensured that actual groundwater, and not stagnant casing water, was being sampled. Wells were purged and sampled using: (1) a peristaltic pump equipped with dedicated polyethylene tubing and foot valves; (2) a whale pump; or (3) by hand using dedicated polyethylene tubing and a foot valve, where depths to water were greater than one atmosphere of pressure and could not be mechanically lifted (*i.e.*, at wells 26 and 29b). During purging and sampling, the tubing and whale pump intakes were placed within, or in close proximity to, the screened interval of each well to ensure that fresh groundwater entering the well was sampled. Groundwater was generally pumped through an open-top bottle, acting as a single-chamber flow-through cell, housing an ORION 250A+ pH and temperature probe. For the observation wells, a Hach sensION6 dissolved oxygen probe was placed within the screened zone of the well and below the tubing or whale pump. For the research wells, the dissolved oxygen probe was placed within the flow-through cell, as the diameter of the dissolved oxygen probe was wider than the diameter of the research wells. All probes were kept out of direct sunlight.

For sampling at the domestic wells, highland wells and the Town of Oliver municipal supply wells, unfiltered and untreated groundwater was collected directly from a tap connected to the well head. For the irrigation user's sample, unfiltered and untreated water was collected directly from a hose connected to an outdoor tap. For sampling at the pumphouses, unfiltered and untreated water was collected directly from taps connected to the lake intake pipes. All taps were turned on for a minimum of 15 minutes prior to sample collection in order to remove any stagnant water within the piping and/or hose.

Field pH and temperature, measured with an ORION 250A+ probe, were recorded at the time of sample collection. Alkalinity was measured by titration to an endpoint of pH 4.3 (for samples containing an alkalinity of up to 500 mg/l as $CaCO_3$) or pH 4.6 (for samples containing an alkalinity of about 150 mg/l as $CaCO_3$) shortly after sample collection (generally, in the evening following sample collection or, occasionally, the next day) using a Hach alkalinity kit with a digital titrator.

Groundwater samples were analyzed for dissolved ions, trace metals, isotopes of water, and/or ^{3}H and ^{14}C age dates. Samples for dissolved ion and trace metals analyses were filtered soon after collection through a 0.45 μm cellulose acetate membrane filter and collected in 250 ml polyethylene bottles. Samples for cation and trace metals analyses were acidified to pH < 2 with 3 ml of HNO_3. Samples for isotopes of water were left unfiltered and collected in 4 or 30 ml polyethylene bottles at the time of sampling. Samples for ^{3}H age dating were left unfiltered and collected in 250 ml polyethylene bottles. Samples for ^{14}C age dating were left unfiltered and collected in 125 ml amber glass bottles filled with mercuric acid to prevent bacterial oxidation. Amber glass bottles were stored in a dark location prior to shipment. All sample bottles were filled so that no, to minimal, headspace remained.

5.3.4 Geochemical Analysis

5.3.4.1 Dissolved Ions and Trace Metals

The following samples within the valley bottom and benchlands were analyzed for dissolved ions and trace metals on up to five occasions in February, June, July and September of 2006 and February 2007: 49 groundwater samples from observation wells, 14 groundwater samples from domestic wells, 14 groundwater samples collected from research wells, and one sample from the irrigation user. A summary of the wells sampled and the sampling date(s) is provided in Table C.1 of Appendix C.

Using ion chromatography, anion analyses (only) were completed by the USGD Aqueous Geochemistry Laboratory on a Dionex IC25 Ion Chromatograph for all February 2006 samples. Dissolved ion and trace metals analyses (including laboratory pH measurements) were completed by SRC Analytical of Saskatoon, SK, for the remaining 2006 and 2007 samples. For samples analyzed by SRC Analytical (using laboratory measurements of pH and alkalinity), charge balances ranged from roughly -2 to +3%, and were within the acceptable range of 5% (Freeze and Cherry, 1979). For samples where field pH and field alkalinity were measured, and both dissolved ion and trace metals analyses were conducted, charge balances ranging from -4 to +4% (with the exception of four samples collected at wells 30, 43 and 44 that exhibited charge balances of 6 to 14%) were calculated using Aquachem 4.0 software from Waterloo Hydrogeologic Inc.

5.3.4.2 Isotopes of Water

The following samples were analyzed for isotopes of water on several occasions between April 2006 and September 2008: (within the valley bottom and benchlands) 67 groundwater samples collected from observations wells, 22 groundwater samples from domestic

wells, 17 groundwater samples from research wells, two samples from the Town of Oliver municipal supply wells, and nine samples from irrigation supplies; and (in the highlands) 12 groundwater samples from domestic wells on Kilpoola Mountain, 39 groundwater samples from domestic wells on Anarchist Mountain, four groundwater samples from domestic wells at Bridesville, one groundwater sample from a domestic well at Mt. Baldy, and three springs. A summary of waters sampled and the sampling date(s) is provided in Table C.1 of Appendix C.

Water samples were analyzed for δ^2H and $\delta^{18}O$ at Environment Canada's National Hydrology Research Center (NHRC) in Saskatoon, SK. Sample analysis was conducted on isotope ratio mass spectrometers (IRMS) between April 2006 and April 2007 and by laser spectroscopy (Lis et al., 2008) between April 2007 and April 2008. Where IRMS was used, δ^2H values were measured by converting the water sample into H_2 gas using the standard Zn reduction technique (Coleman et al., 1982) and $\delta^{18}O$ values were measured using the standard CO_2-water equilibration technique (Epstein and Mayeda, 1953). Results were reported relative to VSMOW in the δ(‰) notation (Equation 2.1). The error in the reported values was ±2.0‰ (IRMS) or ±1.0‰ (laser spectroscopy) for δ^2H and ±0.2‰ for $\delta^{18}O$.

For data collected in the highlands east of Osoyoos, statistical analysis was completed using GraphPad Prism version 5.00 for Windows, GraphPad Software, San Diego California USA, to determine whether δ^2H and $\delta^{18}O$ values from Anarchist Mountain, Bridesville and Mt. Baldy could be grouped together. A Kruskal-Wallis nonparametric test, completed as data were not sampled from populations that followed a Gaussian distribution, indicated that the median δ^2H and $\delta^{18}O$ values of groundwater samples collected on Anarchist Mountain, Bridesville and Mt. Baldy (including the three springs) did not significantly vary ($P<0.05$). δ^2H and $\delta^{18}O$ values of groundwaters on Anarchist Mountain, Bridesville and Mt. Baldy were grouped together.

Statistical analyses were completed using GraphPad Software to determine whether a correlation existed between δ^2H and $\delta^{18}O$ values of highland groundwaters and depth of well (where known) and between δ^2H and $\delta^{18}O$ values of highland groundwaters and the ground surface elevation of each well. Two-tailed, non-parametric Spearman tests indicated that statistically significant correlations existed between δ^2H and $\delta^{18}O$ values and depth of well (r_s = -0.5672 and $p<0.0001$ for δ^2H; r = -0.5361 and p = 0.0003 for $\delta^{18}O$) and between δ^2H and $\delta^{18}O$ values and ground surface (r = -0.6378 and $p<0.0001$ for δ^2H; r = -0.4277 and p = 0.0005 for $\delta^{18}O$).

5.3.4.3 Age Dates

Groundwater samples collected from: (within the valley bottom) domestic well 24 and Town of Oliver municipal supply wells 9 and 10; and (in the highlands) domestic well 22 on Kilpoola Mountain and domestic wells 89 and 90 Anarchist Mountain, were analyzed for an age date using the ^3H age dating method. ^3H age dating was completed on a mass spectrometer at the Noble Gas Isotope Laboratory at the University of Ottawa, Ontario.

Groundwater samples collected from domestic well 24 within the valley bottom, and domestic well 22 on Kilpoola Mountain and domestic wells 89 and 90 Anarchist Mountain, were analyzed for an age date using the ^{14}C age dating method. ^{14}C age dating, including $\delta^{13}C$ analysis, was completed at Rafter Radiocarbon Laboratory at the National Isotope Centre, Institute of Geological and Nuclear Sciences Ltd (GNS Science) in New Zealand. Measurements of ^{14}C were made by direct atom counting using Accelerator Mass Spectrometry analysis and were reported in pmC relative to the US National Bureau of Standards (now NIST) Oxalic Acid standard (HOxI), as defined in Stuiver and Polach (1977). Using mass spectrometry, $\delta^{13}C$ was measured on all samples on the CO_2 gas resulting from sample combustion, and reported relative

to the Pee Dee Belemnite (PDB) reference in the δ‰ notation, where R_{sample} and $R_{standard}$ denote the $^{13}C/^{12}C$ isotopic ratios in the sample and the reference material, respectively. $\delta^{13}C$ values were used to normalize the measured radiocarbon activity to $\delta^{13}C$ = -25‰, as isotopic fractionation of the oxalic acid occurs during preparation for ^{14}C counting (GNS Science, 2008). A conventional radiocarbon age (CRA) was calculated using parameters defined in Stuiver and Polach (1977).

5.3.5 Chemical Modeling

A total of 79 groundwater samples collected from wells within the valley bottom and benchlands, excluding the February 2006 samples as only anions were analyzed, and one irrigation user's water sample, were classified using Aquachem 4.0. Results were then plotted on a Piper drawing. The Saturation Index (SI), a measure of how much of a mineral a groundwater has dissolved relative to how much it can potentially hold (Freeze and Cherry, 1979), was calculated for the same 79 groundwater samples collected from wells within the valley bottom and benchlands using PHREEQC 2.13.1 (Parkhurst and Appelo, 1999).

5.3.6 Other Work

Surface water samples were collected between May 2006 and April 2008 at ten stations along the Okanagan River system (n = 140) and at 15 isolated surface water bodies in the South Okanagan . The samples were collected as part of work completed for this study to satisfy a component of Objective 1 (Stable Isotopes of Hydrogen and Oxygen in Surface Waters in the Okanagan Basin), as described in Chapter 4 of this thesis. Samples were submitted to NWRI for analysis of $\delta^{2}H$ and $\delta^{18}O$ values using the isotope ratio mass spectrometer, as described above. The $\delta^{2}H$ and $\delta^{18}O$ values in surface waters were used in this Chapter to compare to the $\delta^{2}H$ and $\delta^{18}O$ values in groundwaters.

The local meteoric water lines (LMWL) for Osoyoos and West Kelowna, established in Chapter 3 of this thesis (Stable Isotopes of Hydrogen and Oxygen in Precipitation in the Okanagan Basin), were used for comparison of δ^2H and $\delta^{18}O$ values of all waters assessed in this Chapter. Using individual δ^2H and $\delta^{18}O$ values in precipitation, the LMWL for Osoyoos was $\delta^2H=6.06\delta^{18}O-31.21$ and the LWML for West Kelowna was $\delta^2H=7.03\delta^{18}O–12.68$.

Water levels measured by others in: (1) observation wells 26, 28, 30, 35, 39, 72a and 72b on 483 occasions between August 1969 and June 2006 (BC MOE, September 2008; Potter, June 2006); (2) observation wells 42, 43, 44, 54a, 54b, 61, 62a, 62b, 66a, 66b, 70, 74a and 74b on nine occasions between May 2000 and December 2001 (Hi, June 2006); and (3) all observation wells (excluding 42, 43and 44) in September 2004 and July 2005 (Harrington and Kirkland, January 2006), were used in this study. A large number of water level measurements were taken by others, however, only those measured between September 2004 and June 2006 are presented in this Chapter. A summary of the date(s) that water levels were measured is provided in Table C.2 of Appendix C.

Groundwater sampling was conducted in the study area in September 2004 by N. Harrington of the USGD. Eleven observation wells 28, 30, 39, 54a, 61, 62b, 66b, 70, 72a, 72b and 74b were sampled for isotopes of water. Additionally, three observation wells located north of the study area (well 8 completed in a sand and gravel aquifer [Aquifer 257] in Meyer's Flat, west of Vaseaux Lake; and wells 4 and 5 completed in a sand and gravel aquifer [Aquifer 297] in Summerland, adjacent to Okanagan Lake) were sampled for isotopes of water. Locations of these additional observation wells are provided on Figure 5.3. Groundwater samples were collected using sampling methods similar to those described above, with the exception that a three-chamber flow-through cell housing a Hydrolab® multi-probe unit was used to obtain

readings of temperature, pH, electrical conductivity, redox potential and dissolved oxygen concentrations (Harrington, January 2006). Observations wells 28, 30, 39, 61, 62a, 62b, 66a, 70 and 74b were sampled for enriched ^{3}H and $^{3}H/^{3}He$ age dating using sampling methods similar to those described above (J. Hendry, 2006). Results of the isotopes of water and age dating were used in this study.

5.4 Results and Discussion

5.4.1 Water Levels

5.4.1.1 Shallow Groundwaters

Manual water levels measured in shallow groundwaters in the valley bottom and benchlands between September 2004 and February 2007 are presented in Table C.2 of Appendix C. Manual and continuous datalogger measurements collected between 2000 and 2007 are shown on Figure 5.4. For simplicity, and as the annual trend in water levels was generally similar at all wells (except 43, 44, 54a and 54b), only water levels measured at wells 27c and 31b in the North portion of the study area, well 54a in the Central portion of the study area, and well 66a in the South portion of the study area are shown on Figure 5.4. Historical (manual) water level measurements collected between 1969 and 2007 at well 30 (only) are shown on Figure 5.5.

Between 1969 and 2007, water levels in shallow groundwaters of the valley bottom and benchlands (*i.e.*, groundwaters in the glaciofluvial sands and gravels and in the surface of the underlying silt) at all wells, excluding wells 43, 44, 54a and 54b, generally increased between April and September by up to 3 m, reaching a peak during the late summer/early fall, and then decreased during the winter (Figures 5.4 and 5.5). At well 27a, water levels were only recorded by the datalogger in the late summer/early fall when water levels were high enough within the

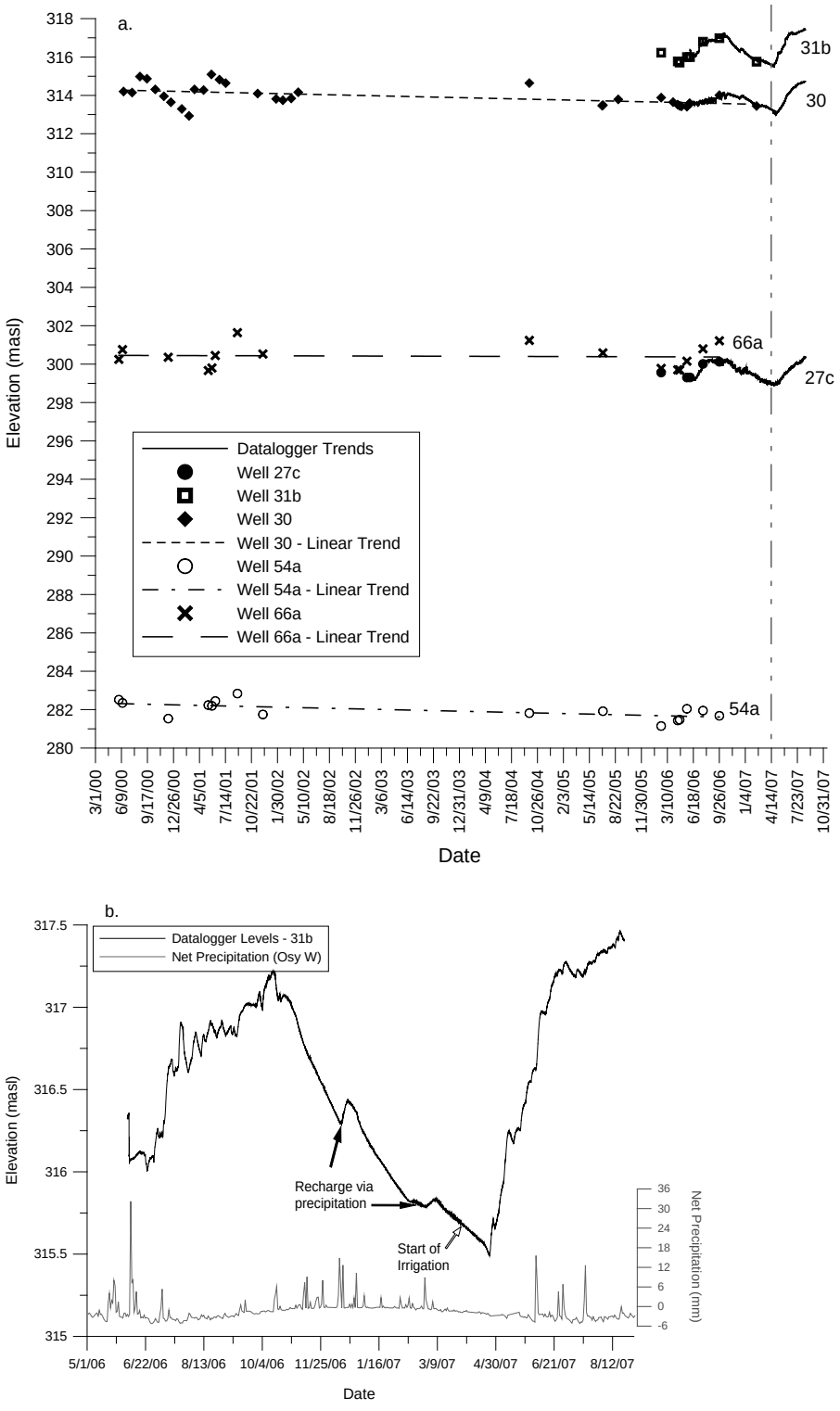

Figure 5.4. a. Manual water level measurements (symbol) and continuous datalogger measurements (solid line) for wells 27c, 30, 31b, 54a and 66a. Linear trends are shown for wells where water level data to 2000 is available (30, 54a and 66a). Vertical dashed line represents the start of irrigation in 2007. b. Rise and fall of water levels at well 31b, predominantly as a function of irrigation. Net precipitation for West Osoyoos, BC, Canada, is shown.

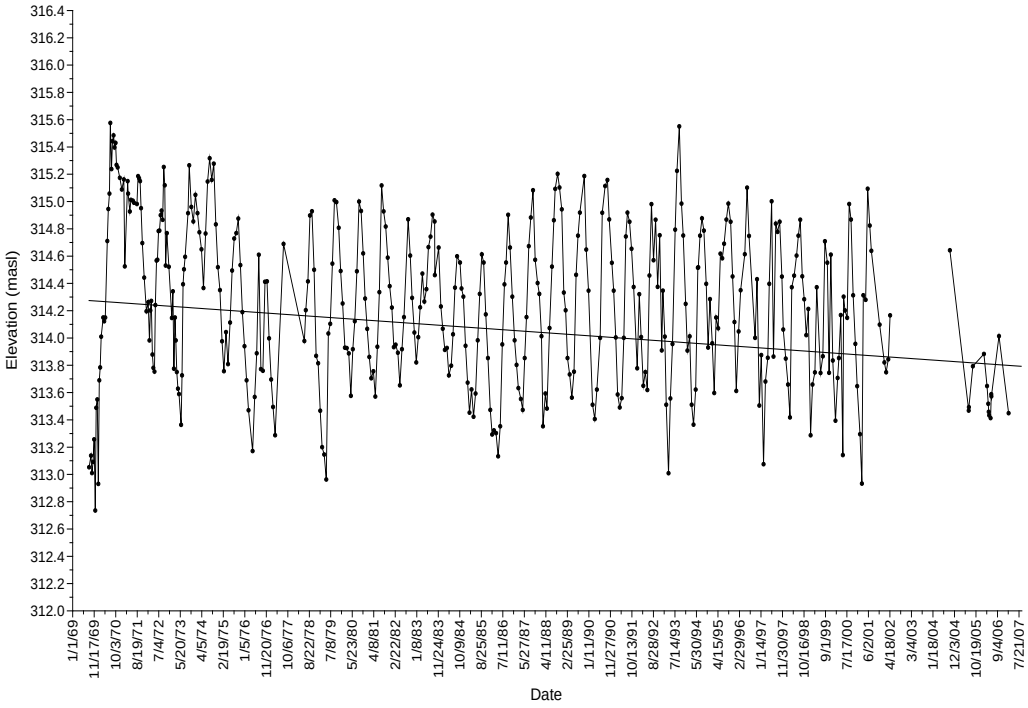

Figure 5.5. Historical water level measurements for well 30. The arrows show the correlation between the application of irrigation water over the spring and summer and groundwater levels over the winter, where higher irrigation rates corresponded to higher water levels over the winter.

well screen to be detected. Water levels fell below the well screen, and, hence, below the datalogger, during winter and spring.

Water levels at all wells (except 43, 44, 54a and 54b) did not exhibit the trend typically observed for recharge of unconfined shallow groundwater by infiltration of precipitation (*i.e.*, increase during spring; decrease during winter) (Freeze and Cherry, 1979). For example, at well 31b in the north portion of the study area, an overall rise in elevation of 1.2 m was observed between June 23 and October 13, 2006 (113 days), followed by an overall decrease in elevation of 1.7 m between October 13, 2006 and April 24, 2007 (194 days), and again by an overall rise in elevation of 2.0 m between April 24 and August 20, 2007 (119 days) (Figure 5.4). For the rise in water levels: assuming that subsurface soils (silt; porosity of 40%) have a specific yield of about 0.1 to 0.2, (Rawls et al., 1982; Twarakavi et al., 2008), infiltration of up to 0.4 m of water

would be required to produce a water level rise of 1.2 m; infiltration of up to 0.7 m would be required to produce a water level rise of 2.0 m. For the increase in water levels, the equivalent infiltration rate is 3.5 mm/day (1.3 m/year) in 2006 and 5.9 mm/day in 2007 (2.1 m/year). Note that an additional 0.5 m of water would be required in both 2006 and 2007 to offset the effects of ET, where ET was calculated by multiplying ET values that are based on a grass reference crop (ETo) by a range of crop coefficients (Kc) for various tree fruits for the months between May and October (BC Ministry of Agriculture Food and Fisheries, 2001)

A total of 29.3 mm of rainfall was recorded for the period between June 23 and October 13, 2006 and a total of 81.2 mm was recorded between April 24 and August 20, 2007. The amount of water falling on the ground as precipitation during these two periods was roughly 7% (in 2006) and 12% (in 2007) of the estimated amount of water infiltrated by irrigation water. Hence, infiltration of precipitation alone was insufficient to produce the water level rises observed in well 31b, or at any of the other wells in the study area. ET rates ranged from roughly 1mm/day in the winter to 6 mm/day in the summer. When accounting for the high rate of ET, and considering that a portion of the precipitation does not reach groundwater due to (1) evaporation prior to entering the soil; (2) uptake by vegetation; and/or (3) retention sin the soil matrix of the unsaturated zone, the amount of precipitation that actually infiltrated the ground surface in the study area was substantially less. Irrigation was, thus, the dominant source of recharge to shallow groundwaters in the study area. Irrigation rates from the Town of Osoyoos Agricultural Metering Pilot Program showed that an average of 1.0 m of irrigation water was applied between April and October 2006, with 0.2 to 0.6 m applied at the two vineyards, and 0.9 to 1.7 m applied at the four orchards (Doucette, September 2008).

Continuous datalogger measurements in 2007 enabled an estimate of the time taken for groundwater levels to respond to infiltration of irrigation water. For example, at wells 27c and 31b, groundwater levels began to rise roughly 9 to 10 days after the start of irrigation on April 15, 2007 (Figure 5.4), indicating that it took up to 10 days for irrigation waters to begin recharging the shallow groundwaters. Note that Environment Canada does not have a complete precipitation data set for West Osoyoos in April 2007, however, it is known that no precipitation fell between April 1 and 4, and only 0.4 mm fell between April 13 and 24 (EC, September 2008b). When considering manual water level measurements alone, infiltration of precipitation appeared to be negligible, particularly during the summer months. However, at some wells, historical increases in shallow groundwater levels were occasionally observed between January and March. For example, at well 30, increases of between 0.5 to 0.7 m were observed in 1983, 1988, 1995, 1996, 1997, 1999 and 2000 (Figure 5.5). The increases in water levels over the late winter indicated that snow-melt initially recharged the groundwaters prior to irrigation. Continuous datalogger measurements showed slight increases shortly after major snow-melt or rainfall events. For example, at well 31b, an increase of 0.14 m (140 mm) was observed between December 14 and 19, 2006, corresponding to infiltrating rain and/or melted snow following temperatures ranging from 1.5 to 10.0°C between December 6 and 14, 2006 (EC, September 2008b) (Figure 5.4). Increases in water levels during the irrigation season from infiltration of precipitation were generally obscured by the effects of irrigation. The smaller peaks and troughs observed within the overall datalogger trends were related to irrigation schedules and not to ET (which would produce diurnal fluctuations) or to infiltration from rain events.

Water levels at wells 54a and 54b, located in the lowest bench, approximately 100 m west of Osoyoos Lake, were variable. In 2001, water levels increased during the summer,

whereas, in 2006, water levels decreased during the summer. Water levels at wells 43 and 44, located adjacent to the west side of Osoyoos Lake, decreased during the summer of 2006. Water levels at wells 43, 44, 54a and 54b were likely affected by lake levels in Osoyoos Lake. Osoyoos Lake levels are regulated by Zosel Dam, located 4 km south of Osoyoos in the US, and by dams and other control structures, as well as surface water withdrawals, in the Okanagan River that flows into Osoyoos Lake from the north.

Where historical water levels were measured, a slight decrease in the overall trend in water levels was observed between 1969 and 2007 in all wells except for well 28, where water levels slightly increased over time, and well 35, where water levels remained relatively constant over time. Changes in water levels were likely due to changes in the amount of irrigation water applied over time, as the trend in water levels over the irrigation season generally corresponded to the trend in water levels over the winter, as shown on Figure 5.5 (*i.e.*, for years where peak irrigation was high, water levels over the winter were also high).

Water levels were not measured at well 38 in the upper benchland, however, the Osoyoos Desert Centre (ODC) who operate the well, indicated that the amount of water available from the well decreases during the summer (ODC, July 2006).

5.4.1.2 Deep Groundwater

Groundwater at well 24 in the deep confined aquifer was flowing artesian. According to the well owner, during well completion, the water level (potentiometric surface) was measured at 1.2 m above the ground surface.

5.4.2 Water Chemistry

Chemical data from groundwater and irrigation water samples are presented in Table C.1 of Appendix C. The concentrations of dissolved species in the groundwater samples were

greater those in the irrigation water sample, indicating that the chemical composition of (irrigation) water was modified during infiltration into the subsurface. The field pH of both groundwaters and the irrigation water sample ranged from 7.0 and 8.0, indicating that the dissolved carbonates in both waters were predominantly in the bicarbonate (HCO_3) form. The pH of groundwaters measured in the field was, on average, 0.8 pH units lower than the pH analyzed by the laboratory (Table C.1 of Appendix C). This is indicative of a higher partial pressure of carbon dioxide (pCO_2) in the groundwater (log pCO_2 of -2.5 to -1.3; Table C.3 of Appendix C) compared to the pCO_2 of the same water in equilibrium with the atmosphere (log pCO_2 of -3.5), and suggests that during groundwater sampling, CO_2 in groundwater degassed upon introduction to the atmosphere, resulting in a small increase in pH.

In general, groundwaters in the study area were mainly a calcium-bicarbonate and calcium-magnesium-bicarbonate type, with sulphate and/or sodium present at high concentrations. Irrigation water was a calcium-magnesium-bicarbonate-sulphate type. The different water types are shown on a Piper diagram (Figure 5.6). The majority of water samples (83%) plot in the same region on the Piper diagram, as shown by the shaded area, indicating similar geochemical composition. This includes 62 of 73 shallow groundwater samples, the three upper benchland groundwater samples and the irrigation user's water sample. The remaining eleven shallow groundwater samples from wells 27c, 29a, 32 and 37 in the north portion of the study area, plot outside of, and to the right of, the shaded area. These samples generally had higher Na, SO_4 and/or Cl concentrations (Table C.1 of Appendix C), possibly the result of local input from fertilizers at orchards and/or active septic fields. Deep confined groundwater also plots outside of, and to the right of, the shaded area. Deep confined groundwater was characterized by higher SO_4, Fe and Mn concentrations (Table C.1 of Appendix C).

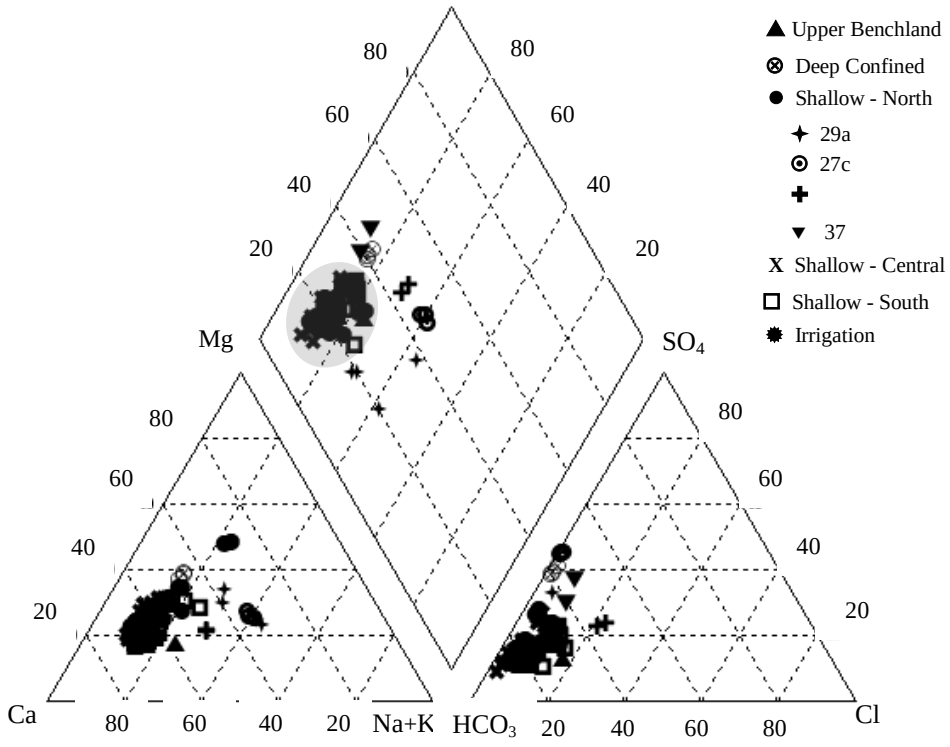

Figure 5.6. Piper diagram showing the chemical composition of shallow groundwater samples, deep confined groundwater samples, upper benchland groundwater samples, and the irrigation water sample, plotted on the basis of the percent of each ion.

Groundwater with SI values of <0 are "under-saturated" with respect to a given mineral phase and indicative of groundwaters that have not dissolved as much of the mineral as they are capable of, or that the mineral is not present; those with SI values of near zero are "saturated" with respect to the mineral phase and indicative of groundwaters that have dissolved as much of the mineral as they can hold; and those with SI values >0 are "super-saturated" with respect to the mineral phase and indicative of groundwaters that are precipitating the mineral from solution (Freeze and Cherry, 1979). SI values near zero or >0 are presented in Table C.3 of Appendix C. In general, most groundwater samples had positive SI values near zero for calcium-based mineral phases (*i.e.*, aragonite, calcite and/or dolomite) and/or for $Fe(OH)_3$. All groundwater samples

had SI values >0 for goethite (FeOOH) and hematite (Fe_2O_3). A total of 10 of the 79 groundwater samples in the north portion of the study area had positive SI values near zero or SI values >0 for rhodochrosite ($MnCO_3$). Groundwaters in the upper benchland generally exhibited greater SI values for aragonite, calcite and dolomite than shallow groundwaters. Deep confined groundwater samples exhibited greater SI values for aragonite, calcite, dolomite, $Fe(OH)_3$, goethite (FeOOH) and hematite (Fe_2O_3), and lower pCO_2 values, than shallow groundwaters.

During field sampling activities, a whitish-yellow precipitate was identified on monitoring equipment (*i.e.*, datalogger wire) present in wells 29, 29a, 30 and 39. Field-grade nitric acid was placed on the precipitate in an attempt to dissolve it and determine whether the precipitate was a calcium carbonate. The precipitate did not dissolve, confirming that carbonates were not super-saturated in the groundwater. The SI for gypsum ranged from -1.20 to -2.15, indicative that gypsum was not present (or that groundwaters were under-saturated with respect to gypsum), however, PHREEQC speciations indicated that another (possibly iron- or manganese-containing) mineral was super-saturated in the groundwater.

Both shallow groundwaters and deep confined groundwater exhibited high specific conductivity and anion concentrations (Table C.1 of Appendix C; Figure 5.7), however, only shallow groundwaters (excluding shallow groundwater in the upper benchland) exhibited elevated nitrate concentrations. Shallow groundwaters with elevated nitrate concentrations were generally located below irrigated orchards in rural areas; some near former and/or currently operating septic fields. Alteration of the original shallow groundwater chemistry likely occurred as a result of application of fertilizers for agricultural purposes and/or subsurface disposal of septic waste, coupled with mixing of irrigation waters.

Groundwater in the upper benchland was distinguished by low to non-detectable concentrations of nitrate, and groundwater in the deep confined aquifer was distinguished by low to non-detectable concentrations of NO_3 and chloride (Cl), indicating that groundwaters in these systems were not susceptible to surface, or near-surface, impacts from agriculture or septic waste disposal. Groundwater in the upper benchland well exhibited elevated Cl and sodium (Na) concentrations. This well is completed in overburden and is located in a non-irrigated area, in close proximity to, and down-gradient of, Highway 3. As NaCl is applied on Highway 3 over the winter (R. Wiens, January 2009), elevated Cl and Na may have been a result of salt application. Both Cl and Na concentrations decreased in the spring as the groundwater was gradually recharged (diluted) by spring rains.

Shallow groundwater wells located in the north portion of study area exhibited higher Na concentrations and lower Ca concentrations than those in the central and south portions of the study area (Figure 5.7). Wells in the north were screened within materials consisting of varying degrees of silt and/or clay, whereas those in the central and south were screened in sand and gravel. Thus, lower Ca and higher Na concentrations may be explained by cation exchange, where, exchange sites on the silt/clay were taken up by Ca^{+2} ions, resulting in a decrease in Ca in groundwater, and Na^{+} ions were released from the exchange sites, resulting in an increase in Na in groundwater.

5.4.3 Age Dating

^{14}C measurements and $\delta^{13}C$, ^{3}H and $H/^{3}He$ isotope values for groundwaters collected in the study area are presented in Table C.1 in Appendix C. Corrections were not made on the reported ^{14}C measurements, as the initial ^{14}C activity (^{14}Co) was not known and insufficient data was available on the bedrock and deep confined aquifers and on carbon sources and sinks in the

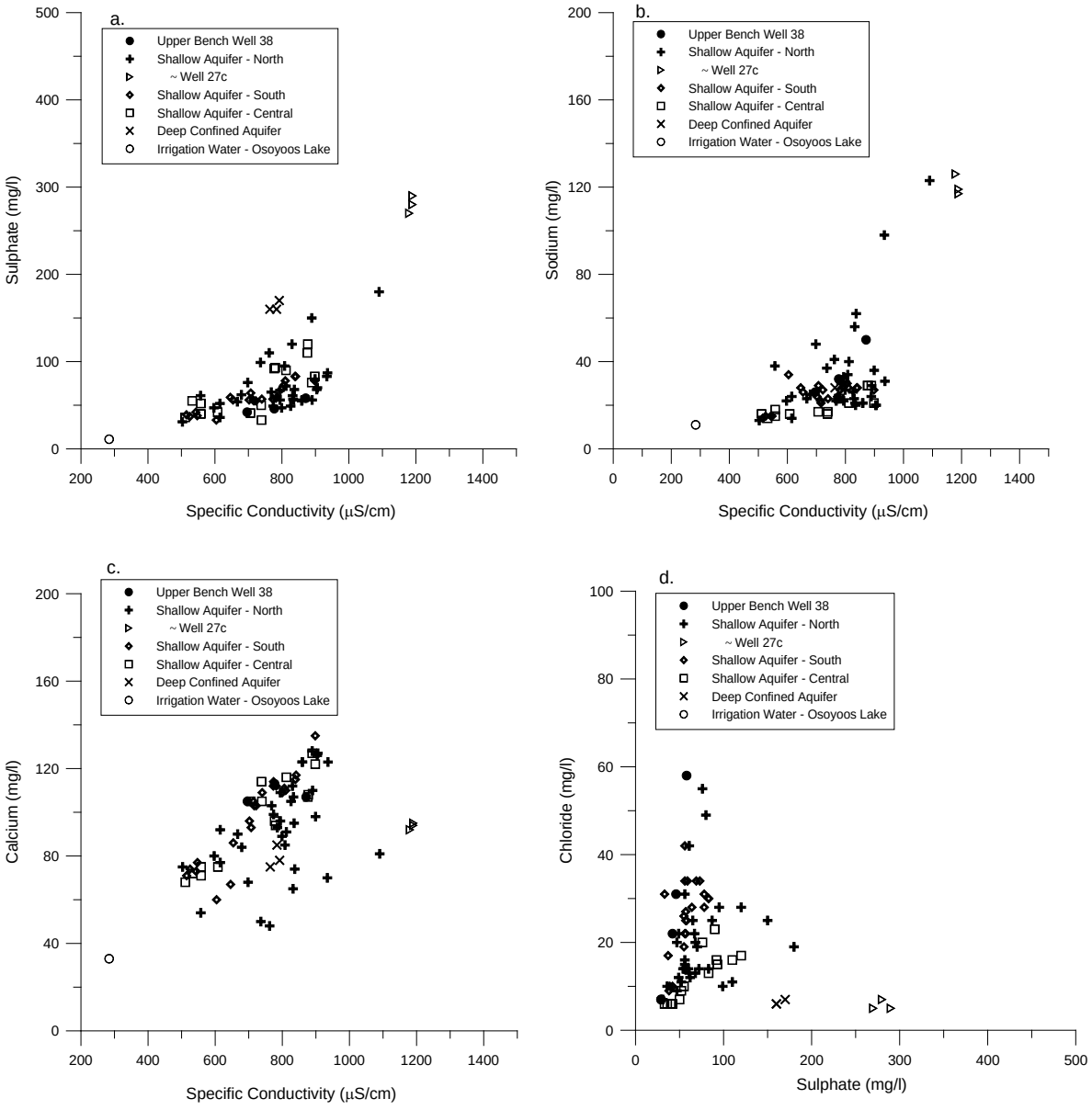

Figure 5.7. a. SO_4 vs. specific conductivity, b. Na vs. specific conductivity, c. Ca vs. specific conductivity, and d. Cl vs. SO_4 for shallow groundwaters, deep confined groundwaters, upper benchland groundwaters and irrigation water.

respective groundwater systems. Having said that, δ^{13}Cvalues can provide important information regarding the environment from which the sample originated (Clark and Fritz, 1997). The δ^{13}C values for bedrock and deep confined groundwaters ranged from -12.3 to -16.4‰ VPDB, and were indicative of groundwaters containing DIC derived from the

dissolution of soil CO_2. Based on the assumptions that ^{14}C atmospheric levels have remained constant through time (Stuiver and Polach, 1977), and that geochemical processes have not significantly diluted the DIC content of the groundwaters analyzed (based on $\delta^{13}C$ values), the true groundwater ages are likely similar to (but not older than) the reported CRAs.

The activity of ^{14}C in the single groundwater sample collected on Kilpoola Mountain (well 22; sample 3) was 67.83 ± 0.17 pmC, with a corresponding CRA of 3,062 ± 20 years before present (BP). The activities of ^{14}C in the groundwater samples collected on Anarchist Mountain were 98.63 ± 0.23 pmC at well 89 (sample 2) and 80.44 ± 0.19 pmc at well 90, with corresponding CRAs of 55 ± 20 years BP and 1,692 ± 20 years BP, respectively. The lower ^{14}C activities at wells 22 and 90 were indicative of the slightly longer residence time of groundwater in the fractures of highland bedrock. The slightly higher ^{14}C activity at well 89 suggested a shorter groundwater flow path from the source. The activity of ^{14}C in the groundwater sample collected from the deep confined aquifer (well 24) was 88.25 ± 0.21 pmC, with a corresponding CRA of 948 ± 20 years BP, and was indicative of the longer flow path that groundwater takes to recharge the deep confined aquifer. For the deep confined aquifer, leakage of water from the overlying aquitard did not appear to be a dominant process, as the ^{14}C activity in the groundwater sample collected at well 24 would have been significantly lower, reflecting the age of the silt deposition some 10,000 to 12,000 years ago.

^{3}H was present in all groundwater samples analyzed, including groundwaters where ^{14}C was present. ^{3}H isotope values of groundwaters in the highlands ranged from 4.2 to 5.3 TU, with a mean of 4.9 ± 0.7 TU. The ^{3}H isotope value of the deep confined groundwater was 13.4 ± 1.0 TU. The presence of ^{3}H and ^{14}C contents in bedrock and deep confined groundwaters suggested mixing of young and older groundwaters. As all three wells sampled (24, 89 and 90) had been

actively used for domestic purposes, the younger groundwater was likely introduced into the respective groundwater systems from pumping activities. Alternatively, as many bedrock wells are completed as open holes, the intersection of a fracture recharged by modern water may have contributed modern water to the bedrock wells.

^{3}H isotope values of shallow groundwaters in the valley bottom and benchlands of Osoyoos and Oliver ranged from 8.7 to 13.7 TU, with a mean of 11.0 ± 1.5 TU. Where analyzed, $^{3}H/^{3}He$ isotope values of shallow groundwaters (with the exception of groundwater at well 39) ranged from 0.2 to 3.3 TU, with a mean of 1.3 ± 1.3 TU. The corresponding age of these groundwaters ranged from 0.4 to 5 years, with a mean of 2.0 ± 1.8 years. Groundwater in well 39 had a $^{3}H/^{3}He$ isotope value of 15.6 TU, corresponding to an age of 13.6 years. Water level responses in well 39 were significantly affected by the application of irrigation water during the study period (*i.e.*, water levels were up to 2 m higher in the summer/early fall than during the winter), and, thus, the ^{3}H and $^{3}H/^{3}He$ content in the groundwater at well 39 should be a record of the length of time elapsed since recharge of irrigation water (Plummer et al., 2004). During field work in 2006, it was noted that the area surrounding well 39 had been converted from a tree fruit orchard to a vegetable (pepper) farm. It is not known whether irrigation continued during this transition period, however, based on the older age of the groundwater at well 39, irrigation may have ceased for some time allowing slightly older (irrigation) water to recharge the area. The ^{3}H concentrations (4.2 to 15.6 TU) and the corresponding ages based on $^{3}H/^{3}He$ dating (0.4 to 5 years; 13.6 years at well 39) were in general agreement with "ball-park" values presented by Motzer (2007).

$^{3}H/^{3}He$ age dates for shallow groundwaters were plotted against the sample collection depth, or groundwater intake zone (Figure 5.8). There does not appear to be a relationship

between $^{3}H/^{3}He$ ages and depth, as in Wassenaar et al. (2006), where an exponential increase in groundwater age with depth was identified at the Abbotsford site, as deep groundwaters were subjected to significantly longer flow paths than shallow groundwaters. The young groundwater ages and the consistency between age date and depth at wells sampled within the study area indicated that a relatively short flow path existed from the infiltration source to the shallow groundwater table. ^{3}H and $^{3}H/^{3}He$ values in shallow groundwaters were consistent with recharge via irrigation water obtained from the Okanagan River system, with a minor component of recharge via recent precipitation.

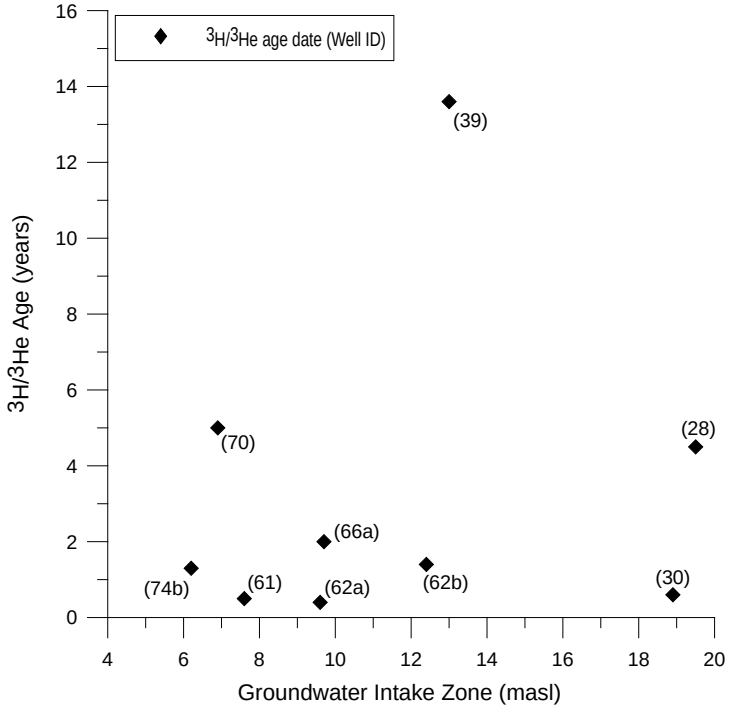

Figure 5.8. $^{3}H/^{3}He$ ages vs. groundwater intake zone for samples collected at wells 28, 30, 39, 61, 62a, 62b, 66a, 70 and 74b in shallow groundwaters of the valley bottom and benchlands.

5.4.4 Isotopes of Water

The $\delta^{2}H$ and $\delta^{18}O$ values of groundwater, spring and irrigation samples collected from the study area are presented in Table C.1 in Appendix C, and plotted on a $\delta^{2}H$-$\delta^{18}O$ diagram (Figure 5.9) along with the $\delta^{2}H$ and $\delta^{18}O$ values of surface water samples collected from: (1)

Peanut Pond and a kettle lake in Osoyoos; (2) Wildhorse, Spotted Lake, Kilpoola Lake, and Blue Lake on Kilpoola Mountain; (3) Haynes Creek, Chapman, Taylor and Yos Pond on Anarchist Mountain; (4) McKinney Creek on Mt. Baldy; and (5) 10 surface water collection stations along the Okanagan River system, including four stations in Osoyoos Lake. The local meteoric water line (LMWL) for Osoyoos is shown on Figure 5.9 for comparison of the δ^2H and $\delta^{18}O$ values of groundwater, spring, irrigation and surface water samples. The LMWL for Kelowna is also shown as most surface waters in the south portion of the Basin (including Osoyoos Lake) originate above the outlet of Okanagan Lake where recharge is via precipitation from the north and central portions of the Basin.

5.4.4.1 Recharge by Winter/Early Spring Precipitation

The δ^2H and $\delta^{18}O$ values of groundwaters in highland bedrock wells on Kilpoola Mountain ranged from -149 to -123‰ (mean of -129 ± 8‰) and -19.6 to -16.1‰ (mean of -16.9 ± 1.1‰), respectively, with the exception of one sample from well 50, where δ^2H and $\delta^{18}O$ values were -67 and -3.5‰, respectively. The δ^2H and $\delta^{18}O$ values of groundwaters in highland bedrock wells east of Osoyoos ranged from -145 to -123‰ (mean of -133 ± 5‰) and -18.9 to -15.5‰ (mean of -16.8 ± 0.8‰), respectively. The δ^2H and $\delta^{18}O$ values of all highland groundwaters plot in the bottom left-hand corner of the δ^2H-$\delta^{18}O$ diagram, in a region between winter and spring precipitation, indicating that highland areas were recharged by a combination of snowmelt and spring precipitation (with the exception of well 50). The slightly more positive δ^2H and $\delta^{18}O$ values of groundwater relative to those of winter precipitation samples (*i.e.*, snow) may be due in part to isotopic enrichment during snowmelt from: 1) evaporation of the snow surface; and/or 2) melting of the snow pack, as described in Clark and Fritz (1997). The relatively consistent range in isotopic composition of snowmelt and spring precipitation in the

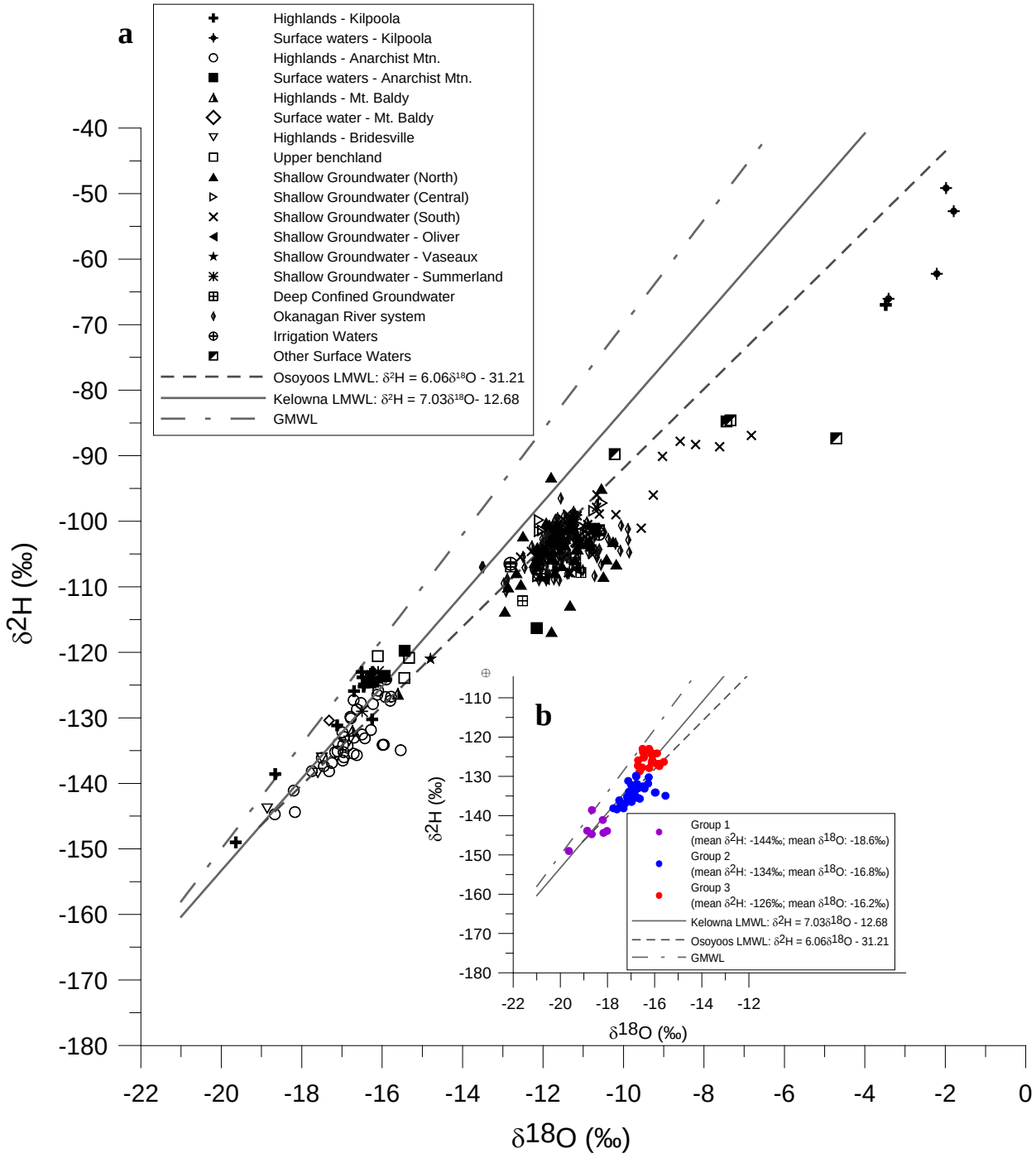

Figure 5.9. a. δ^2H-$\delta^{18}O$ diagram showing: δ^2H and $\delta^{18}O$ values of groundwater, irrigation water and spring samples collected in the study area between February 2006 and September 2008; δ^2H and $\delta^{18}O$ values of surface water samples collected in the Okanagan Basin; and the LMWLs for West Kelowna and Osoyoos and the GMWL (Craig, 1961). b. Close-up of the δ^2H-$\delta^{18}O$ diagram showing δ^2H and $\delta^{18}O$ values of highland groundwaters.

present-day with that of snowmelt/spring precipitation in the last several thousand years may be evidenced by the CRAs of groundwater samples collected in highland bedrock wells.

The δ^2H and $\delta^{18}O$ values of groundwaters in highland bedrock wells east and west of Osoyoos fell into three groups, as shown on the inset of Figure 5.9. The first group consisted of seven samples from seven wells (wells 17 and 19 on Kilpoola; wells 79, 86, 94 and 103 on Anarchist Mountain; and well 56 at Bridesville) where groundwaters exhibited more negative δ^2H and $\delta^{18}O$ values than all other groundwaters. δ^2H and $\delta^{18}O$ values in the first group ranged from -149 to -139‰ (mean of -144 ± 3‰) and -19.6 to -18.0‰ (mean of -18.6 ± 0.5‰), respectively. The second group consisted of 31 samples from 29 wells (wells 16 and 22 [sample 3] on Kilpoola; wells 58, 60, 65, 68, 77, 78, 84, 85, 87, 90, 91, 92, 93 [sample 2], 95, 96 [sample 3], 97, 98, 100a, 100d, 102, 104, 106 and 108 on Anarchist Mountain; wells 45, 53 and 71 at Bridesville; and well 11 on Mt. Baldy) and two springs (81 and 82 on Anarchist Mountain). Groundwater in the second group exhibited δ^2H and $\delta^{18}O$ values that were slightly more positive than those of the first group, ranging from -138 to -130‰ (mean of -134 ± 2‰) and -17.8 to -15.5‰ (mean of -16.8 ± 0.5‰), respectively. Note that groundwater from well 22 (Sample 3) exhibited a CRA of 3,062 ± 20 years BP and groundwater from well 90 exhibited a CRA of 1,692 ± 20 years BP. The third group consisted of 21 samples from 17 wells (wells 18, 20, 22 [samples 1 and 2], 23, 40, 41 and 48 on Kilpoola; and wells 59, 64, 73, 76, 80, 89 [samples 1 and 2], 93 [sample 1], 96 [samples 1 and 2], 100b and 100c on Anarchist Mountain) and one spring (22 on Mt. Baldy). Groundwater in the third group exhibited more positive δ^2H and $\delta^{18}O$ values than all other groundwaters. δ^2H and $\delta^{18}O$ values in the third group ranged from -129 to -123‰ (mean of -126 ± 2‰) and -16.7 to -15.6‰ (mean of -16.2 ± 0.3‰), respectively. Note that groundwater from well 89 (sample 2) exhibited a CRA of 55 ± 20 years BP.

With respect to the correlation between δ^2H and $\delta^{18}O$ values of the highland groundwaters and depth of well, groundwaters exhibiting the most negative δ^2H and $\delta^{18}O$ values may be indicative of: (1) recharge via precipitation falling at higher elevations, or (2) wells that intersect deep fractures that were recharged with older groundwater formed under colder climatic conditions thousands of years ago, with little to no mixing of this older groundwater with young groundwater. If case (2) is true, then one could assume that during recharge of highland groundwaters several thousands of years ago, the isotopic composition of ^2H and ^{18}O in "colder" precipitation was slightly more negative. Groundwater with slightly more positive δ^2H and $\delta^{18}O$ values may be indicative of wells that intersect shallower fractures that were recharged with younger groundwaters. Additional sampling of highland groundwaters for groundwater chemistry and age dates (^3H, $^3H/^3He$ and ^{14}C) would likely resolve this issue.

Surface water bodies on Kilpoola did not appear to be a source of recharge for bedrock in the Kilpoola highlands, as the δ^2H and $\delta^{18}O$ values of surface waters in the Kilpoola area ranged from -67 to -49‰ (mean of -59 ± 8‰) and -3.5 to -1.8‰ (mean of -2.6 ± 0.8‰), respectively. The only exception is the groundwater sample from well 50, where δ^2H and $\delta^{18}O$ values were similar to those of the nearby surface water sample 51 (-66 and -3.4‰, respectively). Surface water from 51 may have been the source of recharge for groundwater at 50. The δ^2H and $\delta^{18}O$ values of the Kilpoola surface waters plot in the top right-hand corner of the δ^2H-$\delta^{18}O$ diagram, indicating that they are highly evaporitic.

Surface water bodies on Anarchist Mountain did not appear to be a source of recharge for most bedrock in the highlands east of Osoyoos. The δ^2H and $\delta^{18}O$ values of surface waters at Haynes Creek, Chapman and Taylor ranged from -125 to -120‰ (mean of -123 ± 3‰) and -16.3 to -15.4‰ (mean of -15.9 ± 0.4‰), respectively. The δ^2H and $\delta^{18}O$ values of surface waters at

Yos Pond were -116 and -12.2‰, respectively. The δ^2H and $\delta^{18}O$ values surface waters on Anarchist Mountain were slightly more positive than the bedrock groundwater, suggesting that some to minor evaporation occurred. McKinney Creek on Mt. Baldy may recharge bedrock in the highlands east of Osoyoos, or alternatively, the creek may be recharged by groundwater. The δ^2H and $\delta^{18}O$ values of McKinney Creek (-130 and -17.3‰, respectively) were within the range of groundwater values.

5.4.4.2 δ-T Relationship

Groundwaters obtained from higher elevations on Kilpoola Mountain, Anarchist Mountain, Bridesville and Mt. Baldy were generally more depleted than samples from lower elevations. This was likely due to the altitude effect, where, at higher elevations, average temperatures are cooler, resulting in precipitation that is isotopically depleted (Clark and Fritz, 1997). Clark and Fritz (1997) have found that the isotopic depletion per 100 m rise in elevation is about -1 to -4‰ for ^2H and -0.15 to -0.5‰ for ^{18}O. Where groundwaters are recharged from higher altitudes, the recharge source can be estimated if the relationship between δ^2H-$\delta^{18}O$ and elevation is known (Koh et al., 2005). The range in δ^2H and $\delta^{18}O$ values of groundwaters in the highland wells suggested that the groundwater originated from snow and/or rain falling at that elevation (*i.e.*, recharge from surface water bodies was likely very minor, if at all). Thus, the relationship between the isotopic composition of precipitation and elevation can conceivably be established for the study area. The δ^2H and $\delta^{18}O$ values obtained from groundwaters collected at the highland wells were plotted against the ground surface elevation of each well (Figure 5.10). The δ^2H and $\delta^{18}O$ values from shallow groundwater in the upper benchland were included in the cross-plot. Linear regression analysis indicated that the depletion per 100 m rise in elevation was about -1.1‰ for ^2H and -0.08‰ for ^{18}O.

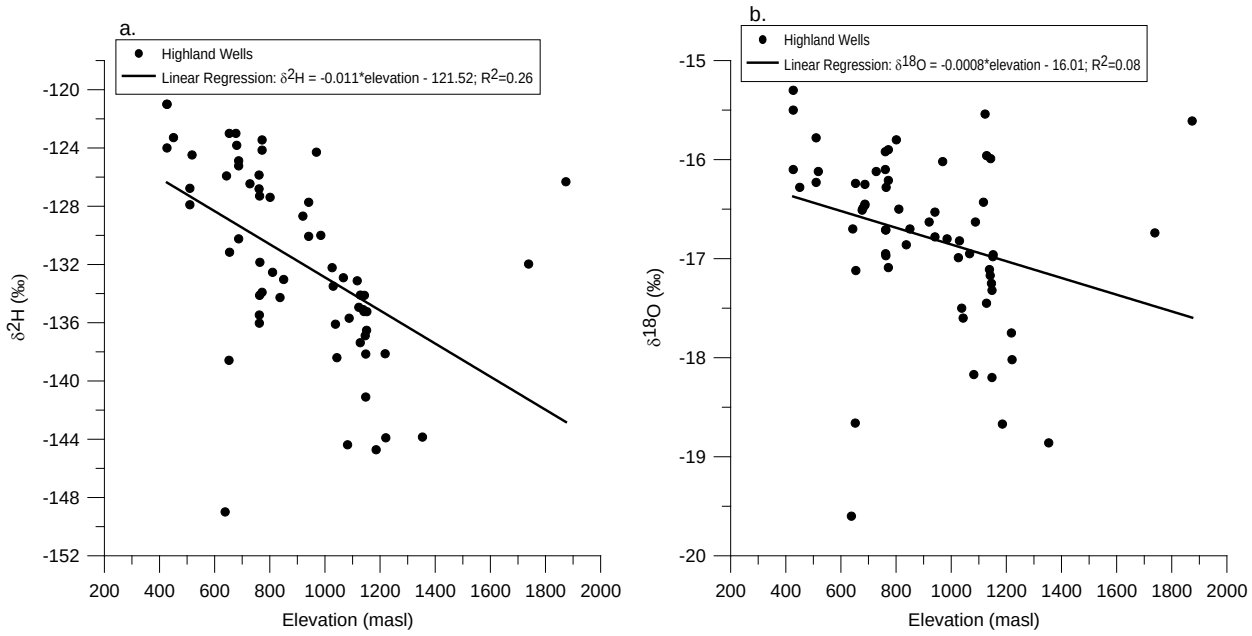

Figure 5.10. Plot showing δ^2H values (a.) and $\delta^{18}O$ values (b.) of groundwater samples collected at wells recharged by precipitation in the highlands and upper benchland vs. ground surface elevations at each well, where available. The relationship is theoretically a function of temperature resulting from the effect of altitude (δ-T).

5.4.4.3 Recharge by Mean Annual Precipitation

The δ^2H and $\delta^{18}O$ values of shallow groundwaters in the upper benchland well ranged from -124 to -121‰ (mean of -122 ± 2‰) and -16.1 to -15.3‰ (mean of -15.6 ± 0.4‰), respectively. The values were more positive than those of groundwaters in the highland bedrock wells indicating that the upper benchland was not recharged by groundwaters from the Kilpoola highlands (Figure 5.9). As the upper benchland is not irrigated, the δ^2H and $\delta^{18}O$ values of groundwaters in the upper benchland represent the mean annual isotopic composition of local precipitation, and, in turn, the isotopic composition of shallow groundwaters for the study area where irrigation is not applied. The mean annual isotopic composition of local precipitation was also represented by shallow groundwaters in wells at Meyer's Flat (58) and Summerland (55 and 56), where δ^2H and $\delta^{18}O$ values ranged from -129 to -121‰ (mean of -124 ± 4‰) and -16.5 to -14.8‰ (mean of -15.8 ± 0.9‰), respectively.

5.4.4.4 Recharge by Irrigation Water

The δ^2H and $\delta^{18}O$ values of shallow groundwaters in the valley bottom and benchlands of the Osoyoos and Oliver areas (excluding six samples obtained near Peanut Pond) ranged from -117 to -93‰ (mean of -103 ± 3‰) and -13.0 to -9.6‰ (mean of -11.5 ± 0.6‰), respectively. The δ^2H and $\delta^{18}O$ values plot just above the middle of the δ^2H-$\delta^{18}O$ diagram, in a region between spring and summer precipitation, and to the right of the LMWL (Figure 5.9). Shallow groundwaters in the study area exhibited δ^2H and $\delta^{18}O$ values that were more positive than those of groundwaters in the highlands and upper benchland, indicating that they were not significantly recharged by groundwater from the highlands, nor from up-gradient sources recharged by mean annual local precipitation.

The δ^2H and $\delta^{18}O$ values of shallow groundwaters were, however, similar to those of irrigation waters and surface waters from Osoyoos Lake. The δ^2H and $\delta^{18}O$ values of irrigation waters ranged from -108 to -101‰ (mean of -105 ± 3‰) and -12.8 to -10.6‰ (mean of -11.7 ± 0.7‰), respectively. The Okanagan River system feeds Osoyoos Lake, the source of irrigation water for the study area, and, as expected, the δ^2H and $\delta^{18}O$ values of irrigation waters plot in a similar region to those of surface waters from the Okanagan River system. The δ^2H and $\delta^{18}O$ values of surface waters from the Okanagan River system ranged from -111 to -98‰ (mean of -103 ± 3‰) and -13.5 to -8.9‰ (mean of -11.5 ± 0.7‰), respectively. The δ^2H and $\delta^{18}O$ values of surface waters of the Okanagan River system, and, in turn, of irrigation and shallow groundwaters in the study area, suggest that evaporation has occurred, as δ^2H and $\delta^{18}O$ values plot to the right of the LMWL for Osoyoos. Note that the small difference in mean δ^2H and $\delta^{18}O$ values of shallow groundwaters (*i.e.*, -103 and -11.5‰, respectively) and irrigation

waters (*i.e.*, -105 and -11.7‰, respectively) may be indicative of isotopic enrichment occurring between the application of irrigation water to the ground surface and its subsequent infiltration to the groundwater table. Some isotopic enrichment may have occurred during the evaporation of irrigation water as it remained on the ground surface prior to infiltration, or from partial evaporation of irrigation water by vapour diffusion during its residence in the top few metres of the unsaturated soil zone (Coplen et al., 2000). Plant transpiration and soil water uptake by plant roots are both non-fractionating processes (Clark and Fritz, 1997).

Extrapolation of the linear regression line for the relationship between isotopic composition of groundwater and temperature due to elevation (Figure 5.10) was completed to identify the theoretical isotopic composition of shallow groundwaters in the valley bottom and benchlands, assuming that they were recharged solely by precipitation and not by groundwaters at higher altitudes. Using an average ground surface elevation of 300 masl, the theoretical δ^2H and $\delta^{18}O$ values of shallow groundwaters in the valley bottom and benchlands would be -125 and -16.3‰, respectively. These theoretical values are more negative than values observed in shallow groundwaters, further supporting that shallow groundwaters in the valley bottom and benchlands were not predominantly recharged by precipitation falling at the elevation of the valley bottom and benchlands.

5.4.4.5 Recharge by Surface Water Sources

Six shallow groundwater samples collected from wells 20a and 20b in the south portion of the study area exhibited more positive δ^2H and $\delta^{18}O$ values than all other samples collected. The δ^2H and $\delta^{18}O$ values for these samples ranged from -96 to -87‰ and -9.3 to -6.8‰, respectively. These samples were collected near Peanut Pond, which itself exhibited δ^2H and $\delta^{18}O$ values that ranged from -87 to -85‰ and -7.4 to -4.7‰, respectively. The data show that

(1) Peanut Pond was an evaporitic surface water body; and (2) the six samples collected from wells 20a and 20b were also evaporitic. As the six samples plot in the same region as samples from Peanut Pond, the evaporated waters of Peanut Pond appear to be the primary source of recharge for wells 20a and 20b. At this time, it is not known whether Peanut Pond is hydraulically connected to Osoyoos Lake, or whether it is recharged by irrigation water applied to nearby residential lawns (Peanut Pond and wells 20a and 20b are located within the Town of Osoyoos) and/or in part by precipitation.

5.4.4.6 Recharge by Other Sources

The δ^2H and $\delta^{18}O$ values of deep groundwater in the confined aquifer ranged from -108 to -106‰ (mean of -107 ± 1‰) and -12.8 to -11.1‰ (mean of -11.7 ± 1.0‰), respectively. Deep groundwater exhibited δ^2H and $\delta^{18}O$ values that were more positive than those of groundwaters in the highlands and upper benchland, but slightly more negative than shallow groundwaters in the valley bottom and benchlands that were predominantly recharged by irrigation water. Age dates of groundwater in the deep confined aquifer were indicative of recharge from a mixture of young and old groundwaters. The deep confined aquifer was likely derived from precipitation that recharged the benchlands up-gradient of, and to the west of, Osoyoos Lake.

5.5 Summary and Conclusions

Recharge of groundwater in highland bedrock was via isotopically-depleted snow-melt and early spring rains. Based on the isotopic composition of highland groundwaters and on CRAs of three groundwater samples, three distinct groundwaters appear to be present in the highlands. Groundwater exhibiting more negative δ^2H and $\delta^{18}O$ values appears to be present at greater depths and may have been recharged several thousands of years ago under colder climate

conditions, when the isotopic compositions of ^{2}H and ^{18}O in precipitation were more negative, or may be recharged by precipitation falling at higher elevations. Groundwater exhibiting slightly more positive $\delta^{2}H$ and $\delta^{18}O$ values appears to be present at shallower depths and may have been recharged by young, warmer groundwaters or precipitation falling at lower elevations. Some groundwaters exhibiting slightly more positive $\delta^{2}H$ and $\delta^{18}O$ values may be representative of a mixture of older and young groundwaters or precipitation falling at multiple elevations.

Recharge of groundwaters in the non-irrigated and undeveloped upper benchland was via mean annual precipitation. The upper benchland was not recharged by groundwater in the bedrock of the Kilpoola highlands, as the isotopic composition of groundwater in the Kilpoola highlands was, on average, 7‰ and 1.3‰ more negative for $\delta^{2}H$ and $\delta^{18}O$, respectively, than that of groundwater in the upper benchland. The slightly more negative $\delta^{2}H$ and $\delta^{18}O$ values in the highlands was a result of the altitude effect. Average $\delta^{2}H$ and $\delta^{18}O$ values of groundwater in the upper benchland (-122‰ and -15.6‰, respectively) represented the mean annual isotopic composition of precipitation in the valley bottom and benchlands of the south Okanagan Basin.

Recharge of the deep confined aquifer occurred up to one thousand years ago, however, the source of the recharge is not known at this time. Additional isotopic data from groundwaters in the deep confined aquifer and, possibly, in the undeveloped benchlands would likely resolve the source of recharge water for the deep confined aquifer. Alternatively, the recharge conditions may have changed since the time of recharge. It is known, however, that recharge was not via groundwater in the highland bedrock of the Kilpoola area, as ^{14}C age dates were different and average $\delta^{2}H$ and $\delta^{18}O$ values in deep confined groundwaters were generally 22‰ and 5.2‰, respectively, more negative than those of groundwaters in the highland bedrock. Furthermore, relatively young ^{14}C age dates suggested that leakage from the overlying aquitard

did not contribute to recharge of the deep confined aquifer. As modern water was identified in the deep confined aquifer, likely from drawdown of groundwaters in shallow aquifer(s) during pumping, mixing with the modern water may have resulted in some dilution of the initial ^{2}H and ^{18}O isotopic composition of groundwater in the deep confined aquifer.

Recharge of shallow groundwaters in the valley bottom and benchlands west of Osoyoos Lake was predominantly via irrigation water that was obtained from the Okanagan River system at Osoyoos Lake. The shallow groundwaters in the valley bottom and benchlands were not recharged by groundwater in the bedrock of the Kilpoola highlands, as the isotopic composition of groundwater in the Kilpoola highlands was, on average, 26‰ and 5.4‰ more negative for $\delta^{2}H$ and $\delta^{18}O$, respectively, than that of the shallow groundwaters. Additionally, precipitation did not significantly recharge shallow groundwaters in the valley bottom and benchlands, as the isotopic composition of mean annual precipitation was, on average, 19‰ and 4.1‰ more negative for $\delta^{2}H$ and $\delta^{18}O$, respectively, than that of shallow groundwaters in the valley bottom and benchlands.

Note, that winter and early spring precipitation should theoretically contribute to recharge of the shallow groundwaters in the valley bottom and benchlands (when ET rates are low). However, the application of irrigation water may effectively attenuate (or, rather, dilute) any precipitation that has infiltrated into the ground surface. The timing of groundwater sample collection for analysis of water isotopes may be a critical variable. For this study, shallow groundwater samples in the valley bottom and benchlands wells were not collected during the period between final snow-melt and the start of irrigation (*i.e.*, sometime in March). Additional isotopic data collected from shallow groundwaters during the period between final snow-melt and the start of irrigation would confirm the extent to which shallow groundwaters were

recharged by snow-melt and early spring rains prior to their recharge by irrigation. The average $\delta^{2}H$ and $\delta^{18}O$ values of shallow groundwaters in the valley bottom and benchlands were similar to those of irrigation waters and surface waters of the Okanagan River system during each sampling event. However, some isotopic fractionation may have occurred during the evaporation of irrigation water as it remained on the ground surface prior to infiltration, or from partial evaporation of irrigation water by vapour diffusion during its residence in the top few metres of the unsaturated soil zone. Shallow groundwaters of the study area were, at the time, continuously recharged by irrigation waters, and the presence of high concentrations of nitrate in the majority of the wells indicated that they were highly susceptible to anthropogenic contamination. Due to the lack of major creeks and tributaries discharging into the Okanagan River system in the South Okanagan Basin (with the exception of Inkameep Creek, northeast of Osoyoos), shallow groundwaters in the South Okanagan Basin are generally not associated with large alluvial fan aquifers. Precipitation falling in the highlands may be recharging deeper or basal valley deposits.

It is important to note that these conclusions were established for the hydrogeological setting of the South Okanagan Basin, where irrigation return flow controls the shallow groundwater dynamics. Although a similar methodology can be used to assess other parts of the Okanagan Basin, recharge environments may not be identical. As an example, in the North and Central Okanagan Basin (where precipitation amounts are greater, ET is lower and catchment areas are much larger), highland surface waters and groundwaters may act as substantially greater recharge sources for groundwaters in the valley. Furthermore, in other parts of the Basin, precipitation may be a more significant source of recharge for groundwaters in the valley.

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CHAPTER 6
CHARACTERIZATION OF NITRATE IN GROUNDWATER IN OSOYOOS, BRITISH COLUMBIA, CANADA

Abstract. In agricultural settings, contamination of groundwater and surface water by nitrate (NO_3) originating from non-point sources is a wide-spread environmental problem. When multiple NO_3 sources are introduced into water supplies, stable isotope analysis of ^{15}N and ^{18}O in NO_3 can be used to differentiate between NO_3 sources, as different sources of NO_3 can have distinct ^{15}N and ^{18}O isotopic compositions. Agriculture is a major economic industry in Osoyoos, British Columbia, Canada. Historically high NO_3 levels have been measured in groundwater, and agricultural drainage systems discharge groundwater from agricultural fields directly into Osoyoos Lake. This study was conducted to characterize NO_3 in groundwaters and agricultural drainage in Osoyoos using stable isotope techniques (^{15}N and ^{18}O of NO_3, ^{2}H and ^{18}O of waters, and ^{18}O of dissolved oxygen in waters). Groundwater samples were collected on up to 5 occasions from 33 wells between February 2006 and February 2007. Drainage from two agricultural drainage systems was collected semi-monthly to monthly at up to 8 locations between March 1997 and November 2002, and May 2006 and April 2008. The results showed that NO_3-N concentrations in groundwaters and agricultural drainage ranged from 0 to 24.4 mg/l. 50% of groundwaters sampled exhibited a decreasing trend in NO_3-N over time, while NO_3-N concentrations in agricultural drainage decreased 3-fold between 1997 and 2008. $\delta^{15}N_{NO3}$ values of groundwaters and agricultural drainage ranged from +1.8 to +15.5‰; $\delta^{18}O_{NO3}$ values ranged from -5.9 to +11.1‰. These data suggested that the groundwaters and agricultural drainage were contaminated by inorganic fertilizer N applied at the soil surface.

Key Words: nitrate, isotopes, groundwater, agricultural drainage, irrigation, fertilizer, volatilization, denitrification.

6.1 Introduction

Nitrate (NO_3) pollution of groundwater is a significant and persistent environmental problem (Blowes et al., 1994; Robertson et al., 2000; Volokita et al., 1996; Wassenaar et al., 2006). NO_3 in groundwater originates from long-term or historical point (*i.e.*, waste lagoons, animal waste storage) and non-point (*i.e.*, fertilizer or manure applications) nutrient sources associated with agricultural practices (Wassenaar et al., 2006). Other causes of NO_3 contamination include irrigation with ammonia-rich effluents discharged by wastewater treatment plants, septic wastewater disposal, and mineralization of crop residue and natural organic materials in soils (Komor and Anderson, 1993; Robertson et al., 2000; Volokita et al., 1996; Wassenaar et al., 2006). Point source contamination of groundwater by NO_3 (*i.e.*, from septic tanks/fields) generally results in contamination as plumes, whereas non-point contamination (*i.e.*, from application of fertilizer) generally results in more widespread, regional impacts on the groundwater quality (Exner and Spalding, 1994; Krapac et al., 2002). NO_3 is highly soluble and has a low cation exchange capacity (CEC), allowing it to travel unimpeded as it does not readily adsorb to soil (Behnke, 1975; Karr et al., 2001). In many poorly-drained agricultural soils, subsurface artificial drainage systems exist that can behave like shallow, direct conduits to surface water bodies (Dinnes et al., 2002). These artificial drainage systems can rapidly transport NO_3 from shallow groundwaters to surface waters, and can result in degradation of surface water quality (Dinnes et al., 2002; Kellman, 2005). As agricultural regions typically receive multiple sources of NO_3, it is critical to identify the source(s) that poses the greatest risk to groundwater and surface water supplies (Bedard-Haughn et al., 2003). However, difficulties arise in differentiating nitrogen (N) sources in larger regional studies due to the coexistence of

multiple anthropogenic sources of N, uncertainty in isotopic fractionation of N, and the uncertainty in the contribution of organic soil N (Hinkle et al., 2007).

It is well known that high levels of NO_3 in drinking water may cause methemoglobinemia, a condition that is characterized by a reduction in the ability of blood to carry oxygen, and that poses a serious risk to infants (Ward et al., 2005). The maximum acceptable concentration of NO_3 in drinking water, set as the Canadian Drinking Water Quality Guideline, is 10 mg/l as nitrate-nitrogen (NO_3-N) (Health Canada, 2008). High levels of dissolved N species in aquatic water bodies may help contribute to eutrophication (Camargo and Alonso, 2006). The Canadian Freshwater Quality Guideline to protect aquatic life is 200 mg/l as NO_3-N, with a 30-day average of less than or equal to 40 mg/l as NO_3-N (Health Canada, 2008).

In the south Okanagan Basin, specifically in and around the Town of Osoyoos, agriculture is one of the major economic industries, and is comprised primarily of fruit orchards and an increasing number of vineyards. Vegetable farms comprise a minor component of the agricultural sector. Elevated levels of NO_3 exist in groundwater and have been inferred to originate from non-point sources associated with inorganic fertilizers from local agricultural practices (BC Ministry of Environment and Environment Canada, 2000; Hodge, 1985; Hodge, 1986; Piteau Associates, 1989). Agricultural drainage systems are present in the northern portion of Osoyoos and discharge water from agricultural fields directly into Osoyoos Lake. This area was chosen for the study because a network of monitoring wells and artificial subsurface drainage infrastructure exist, and the area has historically high NO_3 levels in groundwater.

Stable isotopes of NO_3 (^{15}N and ^{18}O) are used to discriminate between sources of NO_3, as different sources of NO_3 have isotopically distinct ^{15}N and ^{18}O isotopic compositions (Kendall and Aravena, 2000). In most cases, the isotopic composition of ^{15}N and ^{18}O in NO_3 is the

outcome of isotopic fractionations, which occur as a function of the difference in mass of each isotope of N and O, and take place during biologically-mediated reactions (assimilation, nitrification and denitrification) and physical processes (volatilization) in the soil and groundwater zones (Kendall and Aravena, 2000). The combined use of ^{15}N and ^{18}O have been used to evaluate the origin and fate of NO_3 in groundwater (Aravena et al., 1993; Flipse and Bonner, 1985; Hinkle et al., 2007; Moore et al., 2006; Oren et al., 2004; Wassenaar, 1995) and in surface water via subsurface artificial drainage (Deutsch et al., 2006; Dinnes et al., 2002; Kellman, 2005; Magner et al., 2004; Randall and Mulla, 2001). The objectives of this component of the study were to characterize NO_3 in shallow and deep groundwaters and in agricultural drainage systems using stable isotope analysis of ^{15}N and ^{18}O of NO_3 ($^{15}N_{NO3}$ and $^{18}O_{NO3}$, respectively), ^{2}H and ^{18}O of waters ($^{2}H_{H2O}$ and $^{18}O_{H2O}$, respectively), and ^{18}O of dissolved oxygen in waters ($^{18}O_{DO}$).

6.2 Study Area

6.2.1 Location

The Town of Osoyoos and rural areas are located in the South Okanagan Basin of British Columbia, Canada (Figure 6.1). The study area is approximately 7 km long by 1.2 km wide, and is bordered by Osoyoos Lake to the east, mountainous bedrock to the west, and the rural Osoyoos limits to the north and south.

6.2.2 Geology and Hydrogeology

The study area rises up from the valley bottom at Osoyoos Lake, at an approximate elevation of 278 metres above sea level (masl), towards mountainous bedrock in a series of benches that are roughly 20 m high by 200 to 400 m wide. The upper-most bench, at an approximate elevation of 350 masl, rises steeply and contacts bedrock at an approximate

elevation of 450 masl in the north portion of the study area and 400 masl in the south portion of the study area. In general, intermittent sand and gravel outwash terrace and kettled outwash (glaciofluvial) deposits that range in thickness from 1 to 14 m overlie glaciolacustrine silt and/or silt till deposits that are up to 113 m in thickness (Nasmith, 1962; Piteau Associates, 1989), BC MOE, September 2008). The silt deposits transition from brown to grey at depths of greater than 7 m below the top of the silt (BC MOE, September 2008), corresponding to the reduction-oxidation boundary.

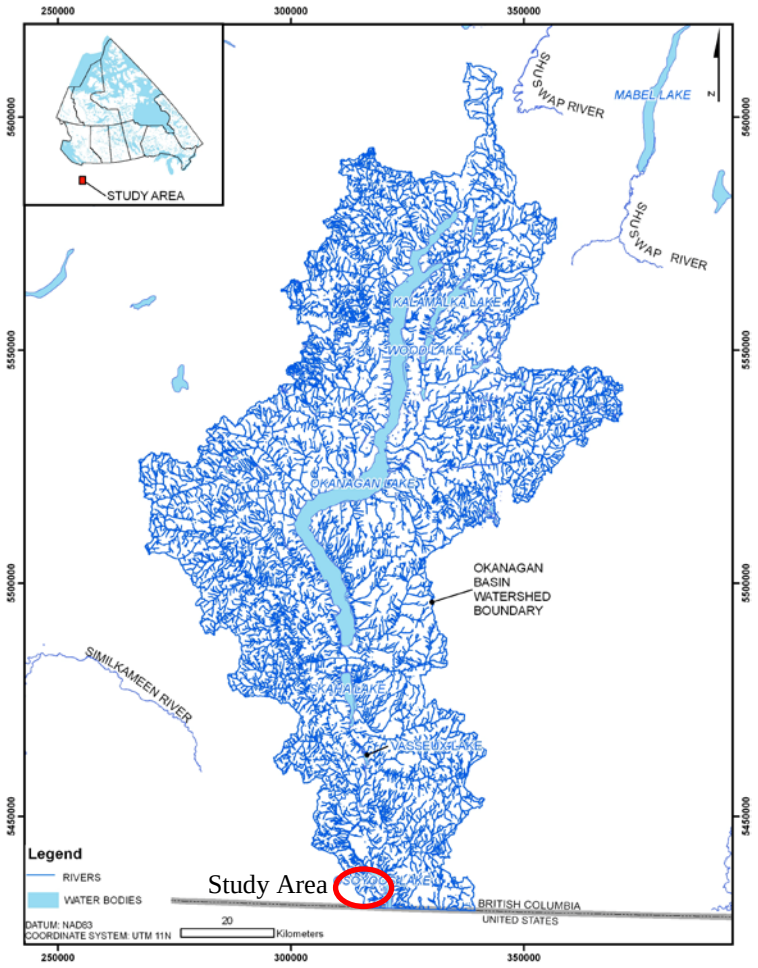

Figure 6.1. Location of study area within the Okanagan Basin, British Columbia, Canada. Map produced using river data from the website www.geobase.ca (National Hydro Network, station 08nm001) and national boundary line and water body data from DMTI Spatial Inc.

Shallow unconfined groundwater is present at the base of the glaciofluvial deposits and in the surface of the silt unit. Shallow groundwater comprises Aquifer 193, a moderately developed aquifer that is highly vulnerable to contamination from surface sources (BC MOE, September 2008). The aquifer extends south across the Canada-U.S. border, however, an assessment of this portion of the aquifer was beyond the scope of this study. A >1.5 m thick layer of confined, water-bearing coarse gravel and cobbles is present below the silt deposits at a depth of roughly 47 m below ground surface in the north portion of the study area (Paley, June 2006). Shallow and deep confined groundwaters in the study area are classified as a calcium-bicarbonate and calcium-magnesium-bicarbonate type, with sulphate and/or sodium present at high concentrations.

Osoyoos Lake receives water from the Okanagan River system, a chain of lakes and respective tributaries that comprise the Okanagan Basin. The lake is the source of irrigation water and some shallow groundwater recharge for the study area.

6.2.3 Agricultural Practices

As a result of the semi-arid climate, tree fruit and grape production is dependent on irrigation. Within the study area, irrigation generally commences in mid-April and continues until mid-October (Doucette and Thomas, May 2006; Doucette and Thomas, September 2008). An Agricultural Metering Pilot Program carried out by the Town of Osoyoos between April and October of 2006 at four orchards and two vineyards showed that irrigation application rates at orchards ranged from approximately 1,400 to 2,700 m^3/hectare (ha) (average of 2,040 m^3/ha), while rates at vineyards were approximately 260 m^3 to 900 m^3/ha (average of 580 m^3/ha), or roughly 1/3rd of the irrigation rates at orchards (Doucette, September 2008). Two agricultural drainage systems, installed decades ago by local residents to improve subsurface drainage, are

present in the northern portion of the study area. The agricultural drainage systems collect groundwater from beneath agricultural lots and discharge it directly into Osoyoos Lake. The total length of each system is approximately 1.5 km, each draining an area of roughly 0.20 km^2 (20 ha; northern system) and 0.15 km^2 (15 ha; southern system).

6.2.4 Potential Nitrate Sources

6.2.4.1 Synthetic Fertilizer

Urea (46-0-0) is the most widely used fertilizer for fruit trees, and is applied on its own and/or blended with a mixed fertilizer (*i.e.*, orchard blend 19-5-17) (Watson, July 2008). Urea is generally applied once in the early spring (*i.e.*, March/April), and for soft fruit trees, again after bloom (*i.e.*, April/May) (Watson, July 2008). Both urea (46 0 0) and NH_4-NO_3 (34 0 0) were reportedly the most commonly used fertilizers in the study area in the late 1980's and early 1990's (Piteau Associates, 1989; York, 1994). The use of NH_4-NO_3 fertilizer (34-0-0) has decreased since circa 2005, and the majority of fruit tree growers no longer use this type of fertilizer (Fossett, October 2008). Ammonium sulphate, calcium nitrate and other orchard blends are also used for fruit tree production (Watson, July 2008). Fruit tree growers, with the exception of apple tree growers, generally apply an annual rate of 220 to 440 kg/ha (Fossett, October 2008). Apple tree growers may apply a lower rate of <60 kg/ha (Watson, July 2008). In terms of N, application of urea to fruit trees corresponds to roughly 30 to 200 kg N/ha. On a typical 4 ha agricultural parcel, an annual application of urea equates to 120 to 800 kg N/year. Urease-inhibited urea is typically applied on grapes at a rate dependent on the soil nutrient conditions, usually around 40 kg N/ha (Fossett, October 2008; Watson, July 2008). Multiple applications of a small amount of orchard blend fertilizer (*i.e.*, 14-16-10) are typically applied on vegetables (about 11 kg N/ha) (Watson, July 2008).

6.2.4.2 Animal and Human Wastes

Application of manure as a source of fertilizer is not a common practice in the study area. Residential lots located within the Town of Osoyoos limits are connected to the municipal sanitary sewer system, while agricultural lots located outside of the Town limits utilize private septic tank and field systems (Doucette, July 2008). Assuming complete oxidation of N to NO_3 in the unsaturated zone beneath a residential septic system, the NO_3-N loading per household was estimated to equal the product of (1) an average residential sewage effluent of 53 mg/l for total N (British Columbia Onsite Sewage Association, 2007); (2) an average effluent generation of 140 l/day, or roughly $1/3^{rd}$ of the average water use per person of 426 l/day (BC MOE, October 2007); and (3) an average person per household of 2.5 (Statistics Canada, October 2008). The potential NO_3-N loading per household was estimated to be roughly 7 kg N/year. This rate is approximately 1% of the total fertilizer N and septic N applied to a typical 4 ha agricultural parcel comprising a soft tree fruit/cherry orchard, and up to 6% of the total fertilizer N and septic N applied to a typical 4 ha agricultural parcel comprising an apple orchard or vineyard.

6.2.4.3 Soil Organic N

A detailed surficial soil survey of the Okanagan Basin conducted in the 1970's indicated that three of the most common soil types in the Osoyoos area (*i.e.*, Haynes, Osoyoos and Skaha) had low amounts of organic matter, as measured by the low (0.7 to 2%) to very low (<0.7%) organic carbon content of the soils (Wittneben, 1986). A very low organic matter content in soils of the study area (0.5 to 1.5%), and an N content in soils insufficient for fruit production, was verified by Brad Fossett, Division Manager of Terralink Horticulture Inc. South Valley Sales (Fossett, October 2008). Soils in the study area are alkaline (Fossett, October 2008).

6.3 Materials and Methods

6.3.1 Groundwater Sampling

Groundwater samples were collected on up to five occasions between February 2006 and February 2007 from observation wells 26, 28, 30, 35, 39, 42, 43, 44, 54a, 54b, 61, 62a, 62b, 66a, 66b, 70, 72a, 72b, 74a and 74b, University of Saskatchewan Geology Department (USGD) research wells 27a, 27c, 29a, 29b and 31b, and/or domestic wells 24, 25, 32, 37, 38, 46, 52 and 57. An irrigation sample was collected from an irrigation user's tap located next to well 29. Sampling locations are shown on Figure 6.2.

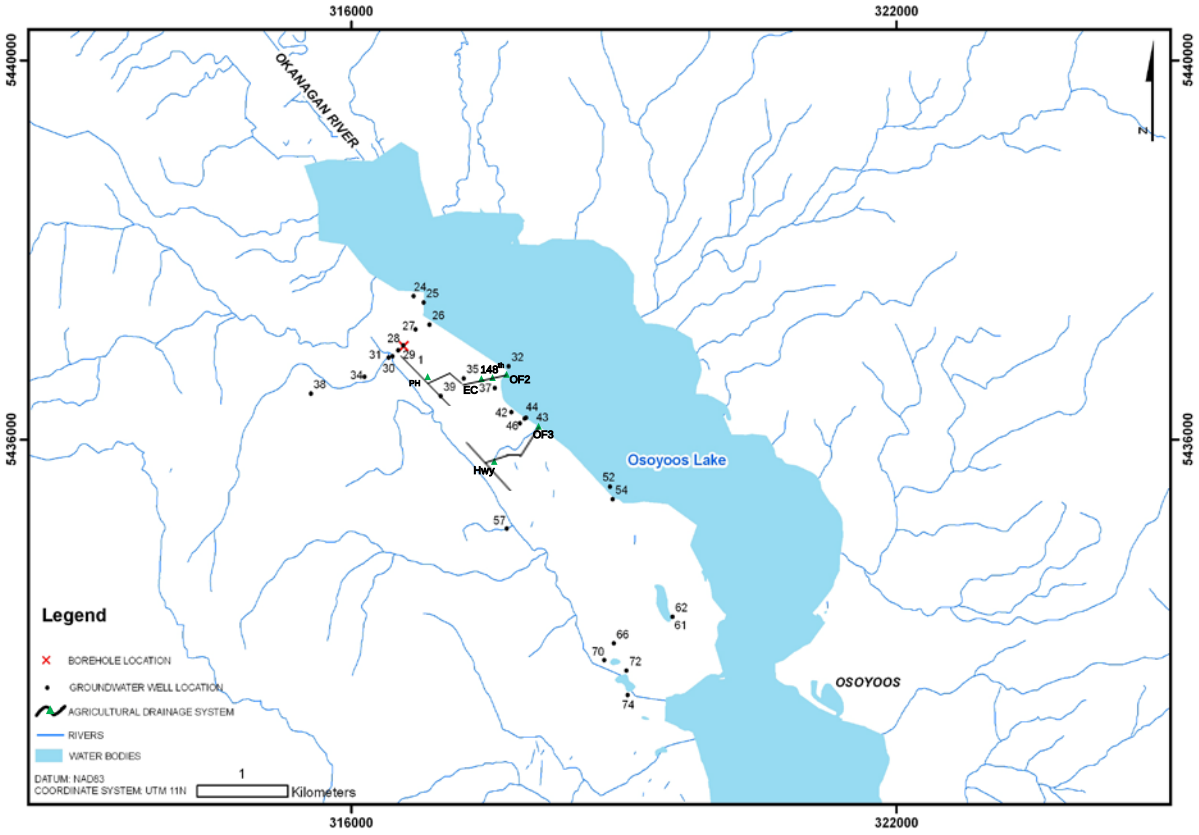

Figure 6.2. Site plan showing location of groundwater wells, agricultural drainage systems: ADS O2 (northern-most) and ADS O3 (southern-most), and the borehole. "PH" includes agricultural drainage system locations PH, PHN and PHS. Map produced using river data from the website www.geobase.ca (National Hydro Network, station 08nm001) and national boundary line and water body data from DMTI Spatial Inc.

Prior to sampling, all observation and research wells were purged until a minimum of three well volumes of groundwater had been removed (or until the wells went dry) and field parameter measurements (pH, temperature and/or dissolved oxygen) had stabilized. This ensured that actual groundwater, and not stagnant casing water, was being sampled. Wells were purged and sampled using: (1) a peristaltic pump equipped with dedicated polyethylene tubing and foot valves; (2) a whale pump; or (3) by hand using dedicated polyethylene tubing and a foot valve, where depths to water were greater than one atmosphere of pressure and could not be mechanically lifted (*i.e.*, at wells 26 and 29b). During purging and sampling, the tubing and whale pump intakes were placed within, or in close proximity to, the screened interval of each well to ensure that fresh groundwater entering the well was sampled. Groundwater was generally pumped through an open-top bottle, acting as a single-chamber flow-through cell, housing an ORION 250A+ pH and temperature probe. For the observation wells, a Hach sensION6 dissolved oxygen probe was placed within the screened zone of the well and below the tubing or whale pump. For the research monitoring wells, the dissolved oxygen probe was placed within the flow-through cell, as the diameter of the dissolved oxygen probe was wider than the diameter of the research wells. All probes were kept out of direct sunlight. For sampling at the domestic wells and the irrigation user's tap, unfiltered and untreated groundwater was collected directly from a tap connected to the well head. Taps were turned on for a minimum of 15 minutes prior to sample collection to remove any stagnant water within the piping and/or hoses.

Groundwater samples were analyzed for dissolved ions, trace metals, isotopes of water, isotopes of nitrate, and/or isotopes of dissolved oxygen. Note that only the parameters NO_3 and Cl are discussed further in this Chapter. Samples for dissolved ion analyses were filtered soon after collection through a 0.45 μm cellulose acetate membrane filter and collected in

polyethylene bottles. Samples for isotopes of water were left unfiltered and collected in 4 or 30 ml polyethylene bottles. Samples for isotopes of NO_3 were filtered soon after sample collection through a 0.45 μm cellulose acetate membrane filter and collected in polyethylene bottles. Samples for isotopes of DO in groundwater were collected following the sampling technique of Wassenaar and Koelher (1999). Samples were collected using a three-way valve connected to a short piece of hosing that was securely fitted onto the end of the whale pump tubing or peristaltic pump tubing so that no air was allowed to enter the hosing. An 0.8mm by 25mm hypodermic needle was attached to the end of the three-way valve. The needle was inserted into a rubber-sealed glass bottle that had previously been evacuated of air and preserved with 35 μl of mercuric chloride to prevent bacteriological consumption of oxygen, and the bottle was approximately 2/3rd filled. All sample bottles were filled so that no, to minimal, headspace remained.

6.3.2 Agricultural Drainage Sampling

Agricultural drainage samples were collected monthly between March 1997 and November 2002 at location EC along agricultural drainage system ADS O2 (Figure 6.2). Agricultural drainage samples also were collected on a semi-monthly basis between May 2006 and November 2006, and on a monthly basis between November 2006 and April 2008, at up to six locations along ADS O2 (OF2, 148th, EC, PH, PHN and PHS) and two locations along system ADS O3 (OF3 and Hwy) (Figure 6.2). Water samples were initially collected from R1 (between EC and O2) and R2 (just southwest of O3) in February 2006, however, these locations were not re-sampled as discharge points closer to Osoyoos Lake were identified. Samples were collected using a stainless steel and/or plastic bucket or a 1L polyethylene bottle. During sample

collection between 2006 and 2008, discharge rates were estimated using a bucket and stop watch at four locations along ADS O2 (OF2, 148th, EC and PHS) and location OF3 along ADS O3.

Agricultural drainage samples collected between 1997 and 2002 were placed in plastic containers, sealed with a tight-fitting lid and frozen. NO_3 concentrations were measured sample collection; isotopes of water and isotopes of nitrate were subsequently analyzed in 2007. Agricultural drainage samples from 2006 to 2008 were collected for dissolved ions, trace metals, isotopes of water and isotopes of nitrate as described in Section 6.3.1 above. Only the parameters NO_3 and Cl are discussed further in this Chapter.

6.3.3 Geochemical Analyses

6.3.3.1 Dissolved Ions

A total of 59 groundwater samples collected from observation wells, 18 groundwater samples from domestic wells and 17 groundwater samples from research wells were analyzed for NO_3 and Cl on up to five occasions in February, June, July and September of 2006 and February 2007. One irrigation water sample from an irrigation user's tap was analyzed for NO_3 and Cl on September 2006. A summary of the locations sampled for NO_3 and Cl and the sampling date(s) is provided in Table D.1 of Appendix D. Using ion chromatography, NO_3 and Cl analyses were completed by the USGD Aqueous Geochemistry Laboratory on a Dionex IC25 Ion Chromatograph for all February 2006 samples. NO_3 and Cl analyses were completed by SRC Analytical of Saskatoon, SK, for the remaining 2006 and 2007 samples. NO_3 concentrations (only) in agricultural drainage samples collected at location EC between 1997 and 2002 were determined colorimetrically using an O.I. Analytical Flow Solution 3000 flow injection analyzer following the manufacturer's procedures at O.I. Analytical College Station in Texas, United States (Neilsen, December 2008).

NO_3-N concentrations in groundwaters collected in February, May, July and September 2006 at wells within agricultural and septic influence (*i.e.*, all wells except 24 and 28), excluding all domestic wells where samples were taken at the tap, were compared to well depth (which generally corresponded to the well intake zone). No statistically significant correlation between NO_3-N concentrations and depth below surface was identified when computed using a two-tailed, non-parametric Spearman test with GraphPad Prism version 5.00 for Windows, GraphPad Software, San Diego California USA (r_s = -0.09, 0.06, 0.32 and -0.22, respectively; P = 0.72, 0.78, 0.41 and 0.31, respectively). A Kruskal-Wallis nonparametric test using GraphPad Software completed as data were not sampled from populations that followed a Gaussian distribution, indicated that the median NO_3-N concentrations of waters collected at all five locations along ADS O2 were not significantly different ($P<0.05$). Thus, NO_3 in agricultural drainage along ADS O2 was considered to be from the same source. A Student`s nonparametric T-test (Mann Whitney) computed using GraphPad Software indicated that the median NO_3-N concentrations of waters collected at both locations along ADS O3 were significantly different. NO_3 in agricultural drainage along ADS O2 was thus not considered to be from the same source.

6.3.3.2 Isotopes of Water

A total of 67 groundwater samples collected from observations wells, 22 groundwater samples from domestic wells and 17 groundwater samples from research wells were analyzed for isotopes of water on up to five occasions in February, June, July and September of 2006 and February 2007. Three irrigation water samples from an irrigation user's tap were analyzed for isotopes of water in May, July and September 2006. A summary of the locations sampled for isotopes of water and the sampling date(s) is provided in Table D.1 of Appendix D.

Water samples were analyzed for δ^2H and $\delta^{18}O$ at Environment Canada's National Hydrology Research Center (NHRC) in Saskatoon, SK. Sample analysis was conducted on isotope ratio mass spectrometers (IRMS) between April 2006 and April 2007 and by laser spectroscopy (Lis et al., 2008) between April 2007 and April 2008. Where IRMS was used, δ^2H values were measured by converting the water sample into H_2 gas using the standard Zn reduction technique (Coleman et al., 1982) and $\delta^{18}O$ values were measured using the standard CO_2-water equilibration technique (Epstein and Mayeda, 1953). Results were reported relative to VSMOW in the δ(‰) notation (Equation 2.1). The error in the reported values was ±2.0‰ (IRMS) or ±1.0‰ (laser spectroscopy) for δ^2H and ±0.2‰ for $\delta^{18}O$.

A Kruskal-Wallis nonparametric test using GraphPad Software indicated that the median δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values of waters collected at all five locations along ADS O2 were not significantly different ($P<0.05$). A Student`s nonparametric T-test (Mann Whitney) computed using GraphPad Software indicated that the median δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values of waters collected at both locations along ADS O3 were not significantly different. Both tests confirmed that the origin of the waters entering their respective agricultural drainage systems was the same.

6.3.3.3 Isotopes of Nitrate

Isotopes of NO_3 were analyzed on 32 groundwater samples collected between February 2006 and October 2006. Isotopes of NO_3 were also analyzed on 74 agricultural drainage samples collected at location EC between March 1997 and November 2002, one agricultural drainage sample collected at location R2 in February 2006, and fourteen agricultural drainage samples collected along ADS O2 and ADS O3 between May and October 2006. NO_3 isotope analysis was completed at the University of Ottawa G.G. Hatch Isotope Laboratories, in Ottawa, Ontario

or at the University of Calgary Isotope Science Laboratory in Calgary, Alberta, on isotope ratio mass spectrometers. $\delta^{15}N$ results were reported relative to atmospheric N (AIR), and $\delta^{18}O$ results were reported relative to the VSMOW standard, in the delta ‰ notation.

6.3.3.4 Isotopes of Dissolved Oxygen

Isotopes of dissolved oxygen were analyzed on 46 groundwater samples collected from 21 wells between February 2006 and October 2006. Analysis of $\delta^{18}O_{DO}$ was completed at Environment Canada in Saskatoon, SK, following the method of Wassenaar and Koelher (1999). Results were reported relative to VSMOW in the delta ‰ notation. DO and $\delta^{18}O_{H2O}$ values were not measured at domestic wells, as water samples were obtained directly from the tap, nor were they measured at wells 26 and 29b, as groundwater samples were collected with tubing (29b) or a bailer (26).

6.3.4 Porewater Analysis

6.3.4.1 Drilling and Soil Characterization

One borehole (1) was advanced in the silt unit to a depth of 15.2 m below ground surface (bgs) on February 16, 2007 using a Geoprobe® 6610 drill rig (Figure 6.2). Continuous 1.5 m length cores were obtained during drilling, and immediately upon recovery, cores were sealed and capped at either end and stored in a cooler. Upon completion of the drilling, the borehole was backfilled with bentonite, and cores were shipped to the University of Saskatchewan, SK, where they were stored at 4°C pending analysis.

Cores were logged for soil type, and pH and Eh were measured along each core using an Orion model 250+ pH meter (n = 86 pH measurements) and an Orion model 250 Eh meter (n = 94 Eh measurements), respectively. Calibration of the Eh and pH probes was completed once daily, prior to commencing measurements, using certified buffer solutions (pH 4, 7 and 10)

and a 420 mV solution with the meter corrected to the standard hydrogen potential, respectively. In all cases, the electrodes were inserted directly in the core samples until a stable reading was obtained (typically 5 minutes).

6.3.4.2 Porewater Sampling and Analysis

Cores were sectioned off into 0.1 m lengths between 1.52 m and 9.1 m, and into 0.2 m lengths below 9.1 m and prepared for porewater extraction and subsequent isotopic and ion analysis. Porewater was extracted from soils using centrifugation. Approximately 50 to 70 g of core sample was placed in the upper chamber of each of four centrifuge cups and centrifuged at 4,000 rpm for 2 hours, with each cup yielding approximately 8 to 10 ml of pore fluids. Two ml of porewater was collected from each section into appropriate vials for analysis of isotopes of water at Environment Canada in Saskatoon, SK, using laser spectroscopy (Lis et al., 2008). Porewater for ion analysis was combined (every 0.2 m for the top 9.1 m, and every 0.8 m below 9.1 m) and collected into sample vials for analysis of major cations and anions at the University of Saskatchewan Aqueous Geochemistry Laboratory using the Dionex IC25 Ion Chromatograph. Only the soil characteristics, NO_3 concentrations in porewater, and isotopes of water in porewater will be discussed in this Chapter.

6.3.5 Fertilizers

Six granular synthetic fertilizer samples utilized in the Osoyoos area (urea, an all-purpose/starter blend, ammonium nitrate, ammonium sulphate, calcium nitrate and an orchard blend) were obtained from TerraLink Horticulture Inc. South Valley Sales in Oliver, BC in April 2006. The samples were analyzed for $\delta^{15}N$ values at NWRI in Saskatoon, SK. $\delta^{15}N$ values of fertilizer N were compared to $\delta^{15}N$ values of groundwaters.

6.4 Other Work

Surface water samples were collected between May 2006 and April 2008 at ten stations along the Okanagan River system (n = 140) and at 15 isolated surface water bodies in the South Okanagan. The samples were collected as part of work completed for this study to satisfy a component of Objective 1 (Stable Isotopes of Hydrogen and Oxygen in Surface Waters in the Okanagan Basin), as described in Chapter 4 of this thesis. Samples were submitted to NWRI for analysis of δ^2H and $\delta^{18}O$ values using the isotope ratio mass spectrometer, as described above. The δ^2H and $\delta^{18}O$ values in surface waters were used in this Chapter to compare to the δ^2H and $\delta^{18}O$ values in groundwaters and agricultural drainage.

The local meteoric water lines (LMWL) for Osoyoos and West Kelowna, established in Chapter 3 of this thesis (Stable Isotopes of Hydrogen and Oxygen in Precipitation in the Okanagan Basin), were used for comparison of δ^2H and $\delta^{18}O$ values in groundwaters and agricultural drainage. Using individual δ^2H and $\delta^{18}O$ values in precipitation, the LMWL for Osoyoos was $\delta^2H=6.06\delta^{18}O-31.21$ and the LWML for West Kelowna was $\delta^2H=7.03\delta^{18}O–12.68$.

Groundwater sampling in the study area was conducted in September 2004 by N. Harrington of the USGD. Eleven observation wells (28, 30, 39, 54a, 61, 62b, 66b, 70, 72a, 72b and 74b) were sampled for chemical parameters and isotopes of water, as described above. Only NO_3 and Cl concentrations and isotopes of water are presented in tabular format and discussed in this chapter. Groundwater sampling in the study area was also conducted by BC MOE and/or EC between August 1985 and June 2006 for major ions and trace metals. BC MOE wells (28, 30, 39, 72a and 72b) were sampled between August 1985 and August 1991, EC wells (42, 43, 44, 54a, 54b, 61, 62a, 62b, 66a, 66b, 70, 74a and 74b) were sampled between August 1985 and June 2006, and one domestic well (46) was sampled between May 2000 and June 2006.

Only NO_3-N, NO_2-N, NH_4, Total Kjeldhal Nitrogen (TKN; ammonia nitrogen + organic N) and/or Cl concentrations are presented in Table D.1 of Appendix D and discussed in this Chapter.

6.5 Results and Discussion

6.5.1 Groundwater

6.5.1.1 NO_3 Chemistry

NO_3-nitrogen (NO_3-N) concentrations in groundwaters are presented in Table D.1 of Appendix D. NO_3-N concentrations at well 38, located up-gradient of agricultural and septic influence, and at well 24, located within the deep confined aquifer, were very low (<0.2 mg/l) to non-detectable (<0.04 mg/l), indicative of minimal to no impact by NO_3 sources. NO_3-N concentrations in groundwaters in the remaining 31 wells ranged from 0 to 24.4 mg/l (mean of 7.1 ± 5.3 mg/l). Of the 31 wells, 12 wells (39%) exhibited NO_3-N concentrations exceeding the Canadian Drinking Water Quality guideline of 10 mg/l as N on at least one sampling event. The widespread distribution of NO_3-N in groundwaters suggests that the NO_3 originated from non-point sources.

In general, NO_3-N concentrations measured between August 1985 and September 2004 were variable. Where NO_3-N concentrations were available from 1985 through 2006, regression analysis on nine wells (26, 42, 43, 61, 66a, 66b, 74a, 74b and 72b) showed NO_3-N concentrations that decreased over time, regression analysis on eight wells (28, 30, 35, 39, 44, 62a, 62b and 70) showed NO_3-N concentrations that increased over time, and regression analysis on one well (72a) showed NO_3-N concentrations that remained relatively unchanged. NO_3-N concentrations over time and linear regression analyses for three representative wells in the study area are shown on Figure 6.3.

The majority of N in groundwaters was in the form of NO_3. NH_3, NO_2-N and TKN concentrations measured in groundwater at up to five observation wells between August 1985 and August 1991 ranged from 0.005 to 0.231 mg/l for NH_3, 0.005 to 0.062 mg/l for NO_2-N, and 0.17 to 0.97 mg/l for TKN (BC MOE, February 2006) (Table D.1 of Appendix D). NO_2-N concentrations measured at 13 observation wells and domestic well 46 in September and December 2001 and in June 2006 were below the detection limit of 0.005 mg/l (Hi, unpublished data). NO_2-N concentrations measured as part of this study at 18 wells in February 2006 were below the detection limit of 0.25 mg/l (Table D.1 of Appendix D).

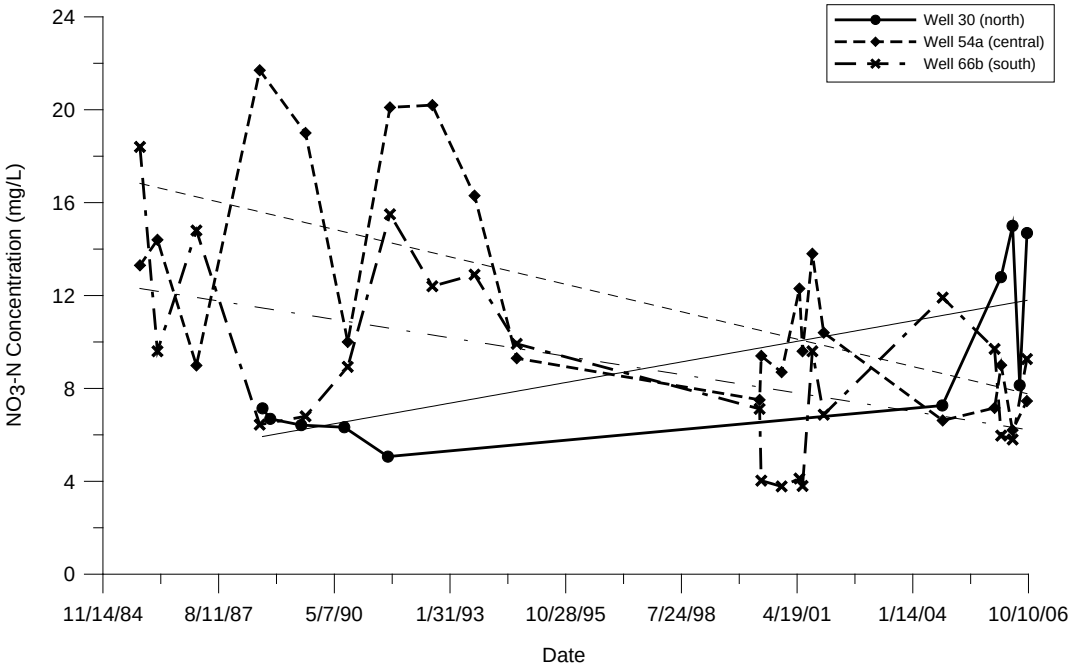

Figure 6.3. NO_3-N concentrations measured between 1985 and 2007 at well 30 in the north portion of study area, well 54a in the central portion of study area, and well 66b in the south portion of study area. Well 30 exhibited an overall increasing trend, while wells 54a and 66b exhibited overall decreasing trends.

No correlation between NO_3-N concentrations in groundwaters at wells within agricultural and septic influence and depth below surface was identified. Wells 28 and 30, completed in the silt unit, were the deepest groundwater wells in the study area, and NO_3-N

concentrations in these wells were among the highest during all sampling events. Rodvang and Simpkins (2001) indicate that NO_3 contamination is common in "*weathered aquitards*" and increases with the presence of fractures. This may be the case here, as both wells were screened in the top of the oxidized silt unit, and well completion logs indicated that some sand and gravel layers were present at well 28 and the silt unit was layered at well 30 (BC MOE, September 2008). Additionally, thin-section analysis of the silt confirmed the presence of very fine sand layers. The penetration of NO_3-impacted groundwater into the top of the silt unit was corroborated with physical and chemical analyses of silt porewater. Eh of porewater ranged from +358 to +664 mV (mean of 526 ± 70 mV), indicative of oxidizing conditions. pH of porewater ranged from 6.9 to 7.7. Eh and pH values fell within the area of NO_3 stability on an Eh-pH diagram. NO_3–N concentrations of porewater ranged from 3.4 to 15.3 mg/l (mean of 9.4 ± 2.1 mg/l). The NO_3–N concentration at the bottom of the silt core (10.9 mg/l at roughly 14.5 mbgs) corresponded to the NO_3–N concentration measured at the nearest groundwater well (28) on September 28, 2006 (9.2 mg/l at roughly 18 mbgs).

Groundwater at wells within potential agricultural/septic influence (all wells except 24 and 38, and wells closest to Osoyoos Lake [42, 43, 44 and 46]), had Cl concentrations that ranged from 7 to 55 mg/l (mean of 22 ± 10 mg/l). Irrigation water used in the study area was chlorinated and itself had Cl concentration of 7 mg/l. The relatively high Cl concentrations in groundwater were indicative of continual recharge by chlorinated irrigation water. In a semi-arid environment, repeated irrigation with chlorinated water and drying may lead to elevated salinity in soils and subsequent Cl leaching into shallow groundwaters (Saysel and Barlas, 2001).

Groundwater at all wells, with the exception of wells 27c, 29a, 35 and 62b, exhibited DO concentrations ranging from 2.4 to 10.2 mg/l during all sampling events, indicative of

aerobic (oxidizing) conditions. Groundwater at wells 27c, 29a, 35 and 62b exhibited DO concentrations ranging from 0.04 to 3.1 mg/l, with the lowest concentrations (0.04 to 1.2 mg/l) observed in May and September of 2006. As low DO concentrations are favourable for denitrification, the low DO concentrations measured in groundwater at wells 27c, 29a, 35, 62a and 62b suggest that local denitrification may have occurred (see Section 6.5.1.4.1).

6.5.1.2 Isotopes of Water

The δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values of groundwaters collected from wells between September 2004 and February 2007 are presented in Table D.1 of Appendix D and plotted on a δ^2H-$\delta^{18}O$ diagram (Figure 6.4). The δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values of: (1) groundwaters and surface waters from highlands to the west (Kilpoola Mountain) and east (Anarchist Mountain, Bridesville, Mt. Baldy) of the study area, (2) surface waters from the Okanagan River system, and (3) surface water bodies within the study area, are included on the δ^2H-$\delta^{18}O$ diagram for reference. The mean δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values in well 38 of the upper benchland (-122 ± 2‰ for δ^2H_{H2O} and -15.6 ± 0.4‰ for $\delta^{18}O_{H2O}$) represented the mean annual isotopic composition of local precipitation, and, in turn the isotopic composition of shallow groundwaters recharged by precipitation in the study area. The mean δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values in the remaining wells, with the exception of wells 24, 29b, 62a and 62b were -103 ± 3‰ and -11.5 ± 0.6‰, respectively. These values were similar to the isotopic composition of irrigation water from Osoyoos Lake. Coupled with peak shallow groundwater levels in the late summer/early fall and $^3H/^3He$ age dates ranging from 0.4 to 5 years (13.6 years at well 39), shallow groundwaters in the study area were recharged via irrigation water with a minor component from recent precipitation. Wells 62a and 62b exhibited more positive δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values, showing direct recharge

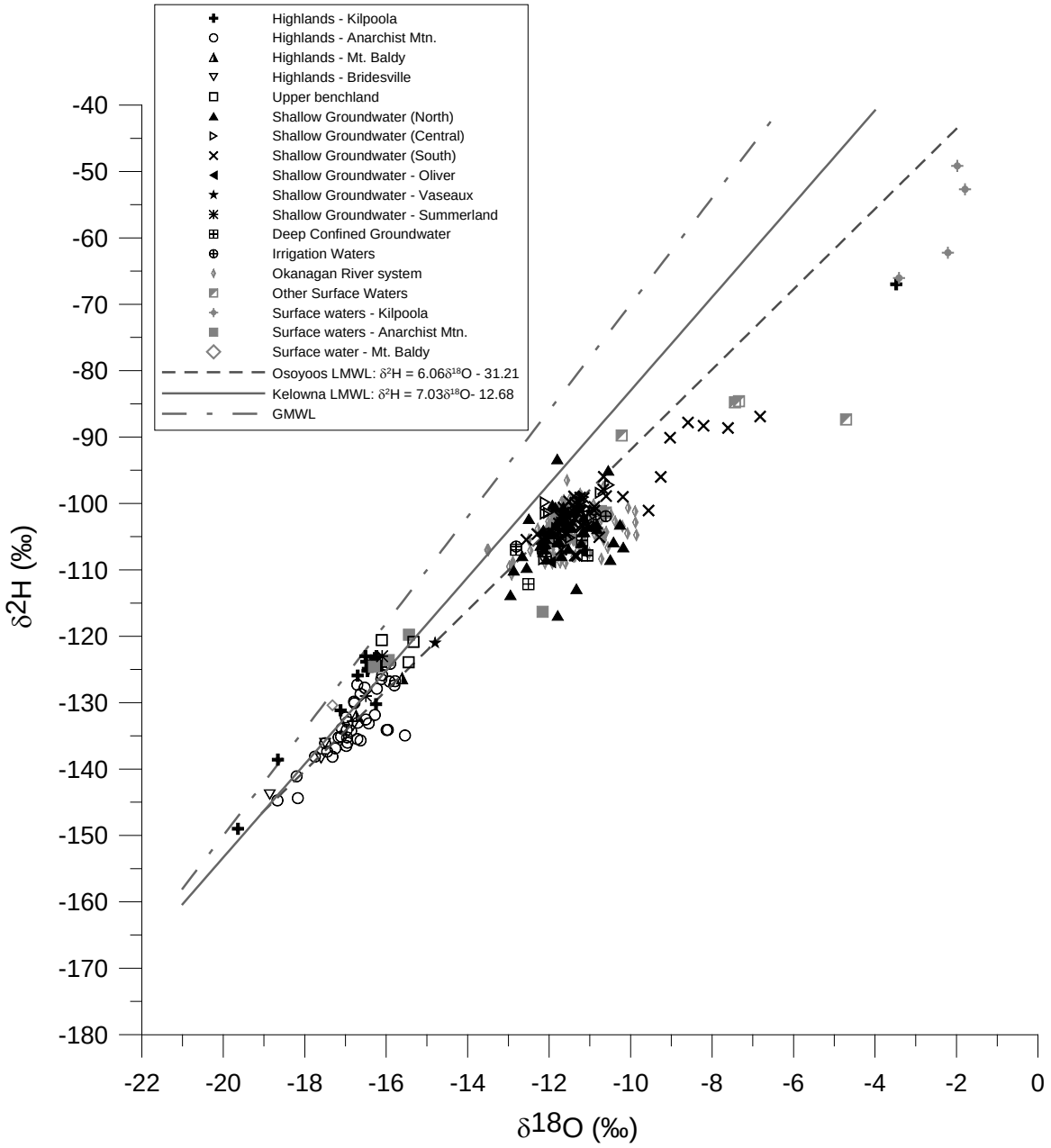

Figure 6.4. δ^2H-$\delta^{18}O$ crossplot showing: groundwaters in the study area plotted relative to the LMWL for Osoyoos, British Columbia, Canada; δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values of surface waters from the Okanagan Basin; δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values of groundwaters and surface waters in the highlands west and east of the study area; δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values of surface waters of the Okanagan River system; the LMWL for Kelowna; and the GMWL (Craig, 1961).

from the nearby evaporative Peanut Pond. Shallow groundwater at well 29b and deep confined groundwater at well 24 exhibited δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values that were slightly more negative than shallow groundwaters, indicating that mixing of recharge sources may have occurred.

The δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values of the silt porewater ranged from -98 to -106‰ (mean of -102 ± 1‰) and -11.4 to -12.4‰ (mean of -11.8 ± 0.2‰), respectively (Table D.2 of Appendix D). The values were within the range of values for shallow groundwaters and irrigation waters, and coupled with NO_3-N concentrations, confirmed that shallow, NO_3-impacted (irrigation) recharge traveled in a vertical direction through the silt unit to depths of at least 18 mbgs. δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values trended toward more positive values from approximately 1.5 to 4.5 mbgs, toward more negative values from approximately 4.5 to 8 mbgs, and toward more positive values from approximately 8 to 14.5 mbgs (Figure 6.5). The trends may be a direct result of temperature changes and/or precipitation changes in the study area. For example, increasing (more positive) δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values may corresponded with: 1) increasing temperatures and a higher degree of evaporation of irrigation waters, which would have resulted in recharge waters with more positive δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values; and/or 2) lower amounts of precipitation, which would have resulted in less influence (*i.e.*, mixing) of groundwaters with colder precipitation having more negative δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values.

6.5.1.3 $\delta^{15}N$ of Synthetic Fertilizers Used in Study Area

The $\delta^{15}N$ values of the synthetic fertilizers used in the study area are presented in Table 6.1. The $\delta^{15}N$ values ranged from -0.4 ‰ to +1.7 ‰ (mean of 0.6 ± 1.4‰). These values were consistent with $\delta^{15}N$ values of fertilizers reported in the literature.

Table 6.1. $\delta^{15}N$ values of fertilizers used in the study area

Fertilizer (N-P-K)	$\delta^{15}N$ (‰)
Urea (46-0-0)	-0.4
All Purpose/Starter Blend (14-16-10-12S)	1.1
Ammonium Nitrate (34-0-0)	1.7
Ammonium Sulphate (21-0-0)	0.0
Calcium Nitrate (15.5-0-0)	1.2
Orchard Blend (19-5-17-6S-3Mg-0.3Zn-0.3B)	0.2

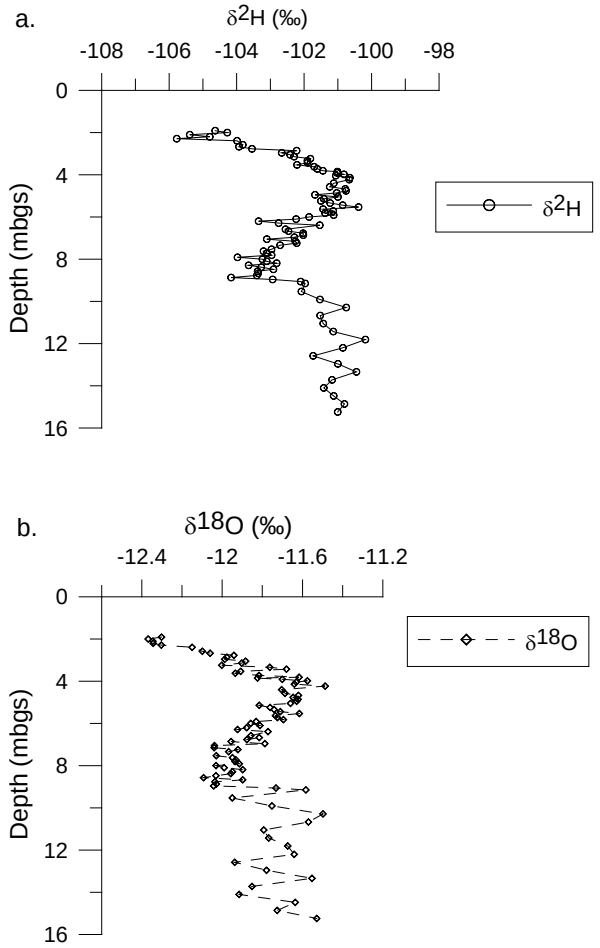

Figure 6.5. a. δ^2H_{H2O} values of silt porewater with depth. b. $\delta^{18}O_{H2O}$ values of silt porewater with depth.

6.5.1.4 Isotopes of NO_3

$\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ values of groundwaters collected between February 2006 and February 2007 are presented in Table D.1 of Appendix D and plotted on a $\delta^{15}N$-$\delta^{18}O$ diagram (Figure 6.6). Also included on Figure 6.6 are the: (1) range in $\delta^{15}N$ values of synthetic fertilizers used in the study area, (2) range in literature $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ values for various other sources of NO_3, and (3) range in calculated $\delta^{18}O_{NO3}$ values for groundwaters in the study area.

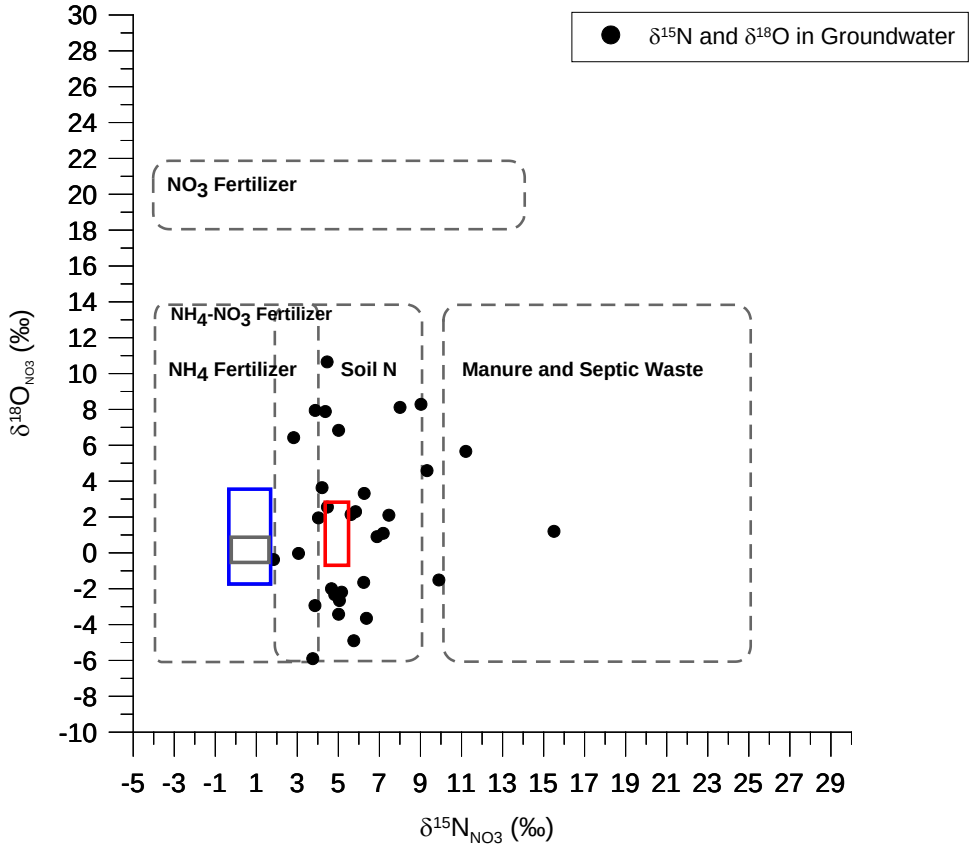

Figure 6.6. $\delta^{15}N$-$\delta^{18}O$ crossplot showing $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ values of groundwaters in the study area. The red box represents the 95% confidence interval (CI) of the sampling mean for $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ values of groundwaters. Dashed lines represent literature $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ ranges for the various NO_3 sources. The blue rectangle represents the range in $\delta^{15}N$ values of synthetic fertilizers used in the study area and the range in calculated $\delta^{18}O_{NO3}$ values for groundwaters in the study area. Within the blue rectangle, the grey rectangle represents the 95% CI of the sampling means for the $\delta^{15}N$ and predicted $\delta^{18}O_{NO3}$ values.

6.5.1.4.1 $\delta^{15}N_{NO3}$

$\delta^{15}N_{NO3}$ values of shallow groundwaters ranged from +1.8 to +15.5‰ (mean of 6.0 ± 2.7‰). Excluding the six highest $\delta^{15}N_{NO3}$ values (+8.0 to +15.5‰) which occurred in groundwater at wells 27c, 29a, 35 and 62b, the range of $\delta^{15}N_{NO3}$ values for the remaining groundwaters was +1.8 to +7.5‰ (mean of +4.9 ± 1.4‰). With the exception of the highest $\delta^{15}N_{NO3}$ values, the distribution of $\delta^{15}N_{NO3}$ values across the study area was relatively consistent, despite the considerable variation in NO_3-N concentrations in groundwater. This is indicative of

the similarity in N source and N transformation processes across the study area (Alva et al., 2006). The lower $\delta^{15}N_{NO3}$ groundwater values were more positive than $\delta^{15}N$ values of the synthetic fertilizers used in the study area, and within the range reported for NO_3 derived from soil organic N (Heaton, 1986; Kendall, 1998).

Mineralization of "native" organic soil N at the study area is considered to be negligible, as most of this N would have been released during the initial years of soil cultivation (Exner and Spalding, 1994). Contributions of "modern" organic soil N to the soil zone from decaying tree matter, plant decomposition (*i.e.*, leaf litter) and crop residues would be minimal. This is a reasonable assumption given: (1) soils in the study area are known to have a low organic matter content; (2) inorganic fertilizer N was applied to the ground surface on an annual basis; (3) the longevity of fruit trees; and (4) crop tillage was not practiced, except for possibly in a small fraction of the study area where vegetable farms are present. As irrigation can rapidly leach NO_3 from the unsaturated zone to the groundwater system (Bohlke, 2002; Fogg et al., 1998), and since a significant amount of irrigation water was applied to the study area, any remaining N in the soils not taken up by plants would undergo nitrification and subsequently be flushed into the shallow groundwater system. The potential for any remaining N to undergo microbial immobilization would be minimized as a result of irrigation and subsequent nitrification. Irrigation is also expected to minimize adsorption of NH_4 onto clay particles in the soil zone.

The source of NO_3 in shallow groundwaters at the study area was, thus, predominantly from the application of inorganic fertilizer N applied at the soil surface. Volatilization of NH_3 from fertilizer N applied as either urea, urea in blended fertilizers, or (historically) NH_4-NO_3 likely occurred during the roughly 6 week period between application and commencement of

irrigation. During this period in 2006 (March 1 to April 15, 2006), irrigation had not yet commenced and conditions were favourable for ammonia volatilization in the alkaline, low soil organic matter soils of the study area. Mean temperatures were 8.1 ºC, with maximum daily temperatures reaching 21.5 ºC, and total precipitation was 50.3 mm (EC, October 2008). Daily average ET was 2.1 mm, with ET reaching a daily average of 3 mm (Farmwest, October 2008). Any ^{15}N-enriched residual N not taken up by fruit trees/vines was the likely subjected to nitrification processes and advanced through the soils into the saturated zone via irrigation water. Nitrification did not result in substantial isotopic fractionation, as the NH_4 pool was oxidized, thus, completing the overall nitrification reaction. Excluding the highest $\delta^{15}N_{NO3}$ values, isotopic fractionation during volatilization raised the $\delta^{15}N$ values from -0.4 to +1.7‰ to within +1.8 to +7.5‰. This is roughly equivalent to an isotopic enrichment factor of up to +7.9‰.

This isotopic enrichment value was consistent with those reported in the literature where groundwaters beneath agricultural sites have greater $\delta^{15}N_{NO3}$ values than those of the fertilizer(s) applied at the surface (Karr et al., 2001; Moore et al., 2006). Flipse and Bonner (1985) showed that NH_3 volatilization of reduced forms of N applied at the Suffolk County, Long Island site resulted in average $\delta^{15}N_{NO3}$ values in groundwater that were up to 12.4‰ higher than the fertilizer source. Spalding et al. (1982) reported an average $\delta^{15}N_{NO3}$ value in groundwater of +3.8‰ at the Burbank-Wallula site as a result of both N fertilizers and mineralized soil N. Aravena et al. (1993) found that $\delta^{15}N_{NO3}$ values in non-septic plume groundwaters at the Cambridge site were higher than those for NO_3 derived from NH_4 and NH_4-NO_3 fertilizers, but within the range of values for NO_3 derived from soil organic N. This was partly attributed to contribution from soil organic N and enrichment in ^{15}N of the NH_4 portion of the NH_4-NO_3 fertilizer during volatilization of NH_3 (Aravena et al., 1993). The lower $\delta^{15}N_{NO3}$ values did not

represent NO_3 derived from septic or manure sources, nor did they represent mixing of NO_3 sources from two end-members, fertilizer and manure.

For two NO_3 sources having distinctive $\delta^{15}N_{NO3}$ values (*i.e.*, fertilizer and manure), the relative contribution of each NO_3 source in a given sample (δ_s) can be calculated using the mixing equation:

$$\delta_s = f_{NO3}\,\delta_{SourceA} + (1-f)\delta_{SourceB} \qquad (6.1)$$

where, f_{NO3} is the proportion of the NO_3 source, and $\delta_{SourceA}$ and $\delta_{SourceB}$ the $\delta^{15}N$ values of groundwater impacted by source A (fertilizer) and source B (manure), respectively. This mixing equation is only practical if the two end-members do not undergo isotopic fractionations either before or after mixing (Kendall, 1998). The equation was applied to the study area to estimate the theoretical $\delta^{15}N_{NO3}$ value of groundwater NO_3, assuming that both septic N and fertilizer N contributed to groundwater NO_3 and that no isotopic fractionations took place before mixing (*i.e.*, during volatilization) or after mixing (*i.e.*, during denitrification). For the equation, an average $\delta^{15}N$ value of 0.6‰ was used for fertilizer N (this study), a $\delta^{15}N_{NO3}$ value of +10‰ was used for septic waste (Aravena et al., 1993), and contributions of septic N and fertilizer N were assumed to be 7 kg N/year (septic N) and 120 to 800 kg N/year (fertilizer N). On a typical 4 ha agricultural parcel, the theoretical $\delta^{15}N_{NO3}$ value of groundwater NO_3 from mixing of septic and fertilizer sources would be between +1.2‰ (δ_s=0.94[+0.6‰] + 0.06[+10‰]) and +0.7‰ (δ_s=0.99[+0.6‰] + 0.01[+10‰]). As the proportion of septic N was very small relative to that of fertilizer N, septic systems were not expected to contribute to NO_3 impacts in groundwater.

Lastly, denitrification did not alter the isotopic composition of N, as (1) $\delta^{15}N_{NO3}$ values in groundwaters were low (< +7.5‰); (2) DO concentrations in groundwaters with low $\delta^{15}N_{NO3}$ values ranged from 3.5 to 9.1 mg/l, indicative of aerobic conditions; and (3) saturation indices of

near zero to > 0 were calculated for oxidized forms of ferrous iron-containing minerals $Fe(OH)_3$, goethite (FeOOH) and/or hematite (Fe_2O_3) in groundwaters with low $\delta^{15}N_{NO3}$ values, and indicative of oxidizing conditions.

The higher $\delta^{15}N_{NO3}$ values of groundwater at wells 27c, 29a, 35 and 62b (i.e., +8.0 to +15.5‰) were: (1) within the range, or towards the low end of the range, of $\delta^{15}N_{NO3}$ values reported for NO_3 derived from manure and septic waste; or (2) along a denitrification trend for NO_3 derived from synthetic fertilizers or organic soil N. $\delta^{15}N_{NO3}$ values at the lower end of the range of values for NO_3 derived from septic waste have been attributed to limited ammonia volatilization of septic waste in the septic tank or below the septic field (Aravena et al., 1993). High Cl^- concentrations are generally indicative of contamination by septic waste, and typically form a 2:1 ratio with NO_3 (Harman et al., 1996). However, high Cl^- to NO_3 ratios may not always be a good indicator for groundwater contaminated by septic waste, as denitrification, for example, may decrease the NO_3 concentration in groundwater relative to the Cl^- concentration. Chloride concentrations at a 1:1 ratio with NO_3 (as NO_3) were observed at wells 29a and 35, while low Cl^- concentrations were observed at wells 27c and 62b. Based on the relatively low Cl^- to NO_3 ratio, it does not appear that these groundwaters were contaminated by septic waste. All samples that exhibited high $\delta^{15}N_{NO3}$ values exhibited low DO concentrations (<1.5 mg/l). Provided that denitrifying bacteria and an electron donor were available, some local denitrification may have occurred around these wells.

6.5.1.4.2 $\delta^{18}O_{NO3}$

$\delta^{18}O_{NO3}$ values of groundwaters ranged from -5.9 to 10.7‰ (mean of 1.7 ± 4.4‰). The values were less than those of NO_3 fertilizers and of NH_4-NO_3 fertilizers. $\delta^{18}O_{NO3}$ values were consistent with NO_3 originating from nitrification of reduced forms of N (*i.e.*, NH_4). Using

Equation 2.20 and the following parameters: (1) $\delta^{18}O_{DO}$ values measured for 41 groundwater samples in the study area (this excludes two samples where local denitrification may have occurred); and (2) $\delta^{18}O_{H2O}$ values for groundwaters where $\delta^{18}O_{DO}$ was measured, the expected $\delta^{18}O_{NO3}$ values for groundwater in the study could range from roughly -2.0 to 3.5‰ (Table D.1 of Appendix D). The measured $\delta^{18}O_{NO3}$ values were generally within the range of calculated $\delta^{18}O_{NO3}$ values, with the exception of seven (7) groundwater samples, where $\delta^{18}O_{NO3}$ values were more positive (Table D.1 of Appendix D). For thirteen (13) samples where ***both*** $\delta^{18}O_{NO3}$ and $\delta^{18}O_{DO}$ were measured, the measured $\delta^{18}O_{NO3}$ values were individually compared to the calculated $\delta^{18}O_{NO3}$ values. In all but two samples, the measured $\delta^{18}O_{NO3}$ values were consistently higher than the predicted $\delta^{18}O_{NO3}$ values (Table D.1 of Appendix D).

The difference in measured and calculated $\delta^{18}O_{NO3}$ values may be attributed to differences in the proportion of the oxygen source (water vs. atmospheric oxygen) during nitrification (Aravena et al., 1993; Mayer et al., 2001). In order for the calculated $\delta^{18}O_{NO3}$ values to agree with measured $\delta^{18}O_{NO3}$ values, slightly less than two oxygen derived from oxygen in water molecules and slightly more than one oxygen derived from oxygen would be required Alternatively, Wassenaar (1995) reported lower $\delta^{18}O_{NO3}$ values at the Abbotsford site as a result of nitrification of residual recharge and soil water with higher $\delta^{18}O$ values after having undergone additional evaporative enrichment during the summer. This may be the case at the study area, as all samples exhibited lower than expected $\delta^{18}O_{NO3}$ values. For the seven samples where measured $\delta^{18}O_{NO3}$ values were significantly higher, mixing of nitrified NO_3 from ammoniacal fertilizer N with NO_3 originating from NO_3 fertilizer and/or NH_4-NO_3 fertilizer likely occurred (Karr et al., 2001). In this case, the $\delta^{18}O_{NO3}$ values of NO_3 originating from NO_3

fertilizer and/or NH_4-NO_3 fertilizer would be preserved as the NO_3 would have been rapidly transported down to the shallow groundwater system during irrigation without alteration of its $\delta^{18}O_{NO3}$ due to immobilization-remineralization processes.

6.5.2 Agricultural Drainage Systems

6.5.2.1 Discharge Rates

Discharge rates, Q, at the discharge point of ADS O2 into Osoyoos Lake (*i.e.*, OF2) and at EC ranged from 2 to >18 L/s. Discharge rates at 148th ranged from 1 to 2 L/s. Discharge rates at the discharge point of ADS O3 into Osoyoos Lake (*i.e.*, OF3) ranged from <0.2 to 8 L/s. Discharge rates generally increased over the summer/early fall and decreased over the winter/spring, corresponding to the irrigation cycle (Figure 6.7).

A water balance was estimated for areas artificially drained by agricultural drainage systems using the parameters provided in Table 6.2 and the following equation modified from Freeze and Cherry (1979)

$$P_{ADS} + I_{ADS} = Q_i + ET_{ADS} + \Delta s_g \quad (6.2)$$

where P_{ADS} is precipitation, I_{ADS} the irrigation applied to ground, Q_i the subsurface artificial drainage, ET_{ADS} the evapotranspiration, and Δs_g the change in storage of the groundwater reservoir. For this approximation, Q_i is the sum of the average monthly discharge rates measured at the discharge point of each agricultural drainage system, and ET_{ADS} is approximately 83% of the total precipitation (Okanagan Water Stewardship Council, 2008). In the area artificially drained by ADS O2, input (315,440 m^3) ≈ output (309,120 m^3), indicating that the majority of water entering the subsurface in the area artificially drained by ADS O2 was discharged into Osoyoos Lake via ADS O2. The small difference in input relative to output may be due to the uncertainty in the size of the drainage area, or may indicate that a minor component of input

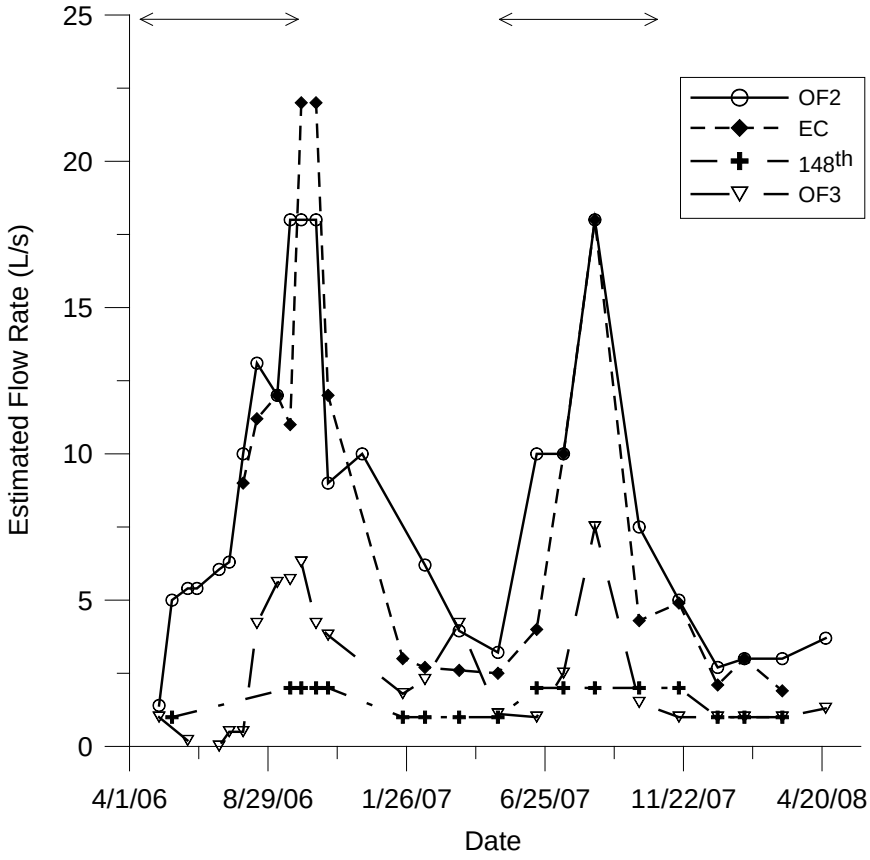

Figure 6.7. Discharge rates measured at the discharge point of ADS O2 into Osoyoos Lake (OF2), at EC and 148th along ADS O2, and at the discharge point of ADS O3 into Osoyoos Lake (OF3). Discharge rates generally increased over the summer/early fall and decreased over the winter/spring, corresponding to the irrigation cycle. The duration of the irrigation period in 2006 and 2007 is shown as ↔.

recharges the shallow groundwater system ($\Delta s_g \approx 6{,}320$ m^3). In the area artificially drained by ADS O3, input (233,430 m^3) >> output (104,050 m^3). The large difference (129,380 m^3) may be due to a significant loss of input to the shallow groundwater system, or, more likely, imprecise estimations of parameters I_{ADS} and Q_i.

Table 6.2. Parameters used for water balance estimates in artificially drained areas, where P_{ADS} is precipitation, ET_{ADS} the evapotranspiration, I_{ADS} the irrigation applied to ground, and Q_i the volume of subsurface artificial drainage.

ADS	**Estimated drainage area (m^2)**	**P_{ADS} over drainage area (m^3)**	**ET_{ADS} over drainage area (m^3)**	**Average I_{ADS} over drainage area (m^3)**	**Avg. Q_i (m^3)**
O2	202,340 (20 ha)	55,440	46,020	260,000	263,100
O3	149,700 (15 ha)	41,030	34,050	192,400	70,000

6.5.2.2 General Chemistry

Waters collected at ADS O2 and ADS O3 between February 2006 and April 2008 were analyzed using Aquachem 4.0, Waterloo Hydrogeologic Inc. Agricultural drainage system waters were a Ca-Mg-HCO_3 type, with the exception of waters collected at 148th and eleven (11) water samples collected at OF2, which were a Ca-Mg-HCO3-SO4 type. Agricultural drainage system waters were compared to groundwaters in the study area between February 2006 and February 2007, and to irrigation supply water collected in September 2006. Agricultural drainage system water, groundwater, and irrigation water types are classified using a Piper diagram (Figure 6.8). Agricultural drainage system waters plot in the same region on the Piper diagram as groundwaters and irrigation supply waters, indicating that agricultural drainage systems both collect and drain groundwaters that have been recharged by irrigation water.

6.5.2.3 NO_3 Chemistry

NO_3-N concentrations in waters along ADS O2 and ADS O3 are presented in Table D.3 of Appendix D. In general, NO_3 concentrations were greater than Cl- concentrations (where measured), as expected from a predominantly agricultural source, and not a septic or manure source.

6.5.2.3.1 ADS O2

NO_3-N concentrations along ADS O2 ranged from 1.4 to 9.3 mg/l (mean of 6.5 ± 1.6 mg/l) at the discharge point into Osoyoos Lake (*i.e.*, OF2), 1.5 to 9.9 mg/l (mean of 6.4 ± 2.0 mg/l) at EC between 2006 and 2008, 6.1 to 8.5 mg/l (mean of 7.2 ± 0.7 mg/l) at 148th, and 4.7 to 20.0 mg/l (mean of 10.6 ± 5.2 mg/l) at locations PH, PHN and PHS. NO_3-N concentrations measured at OF2 and EC generally decreased in the summer/early fall and increased in the winter/spring (Figure 6.9). Lower NO_3-N concentrations in the summer/early

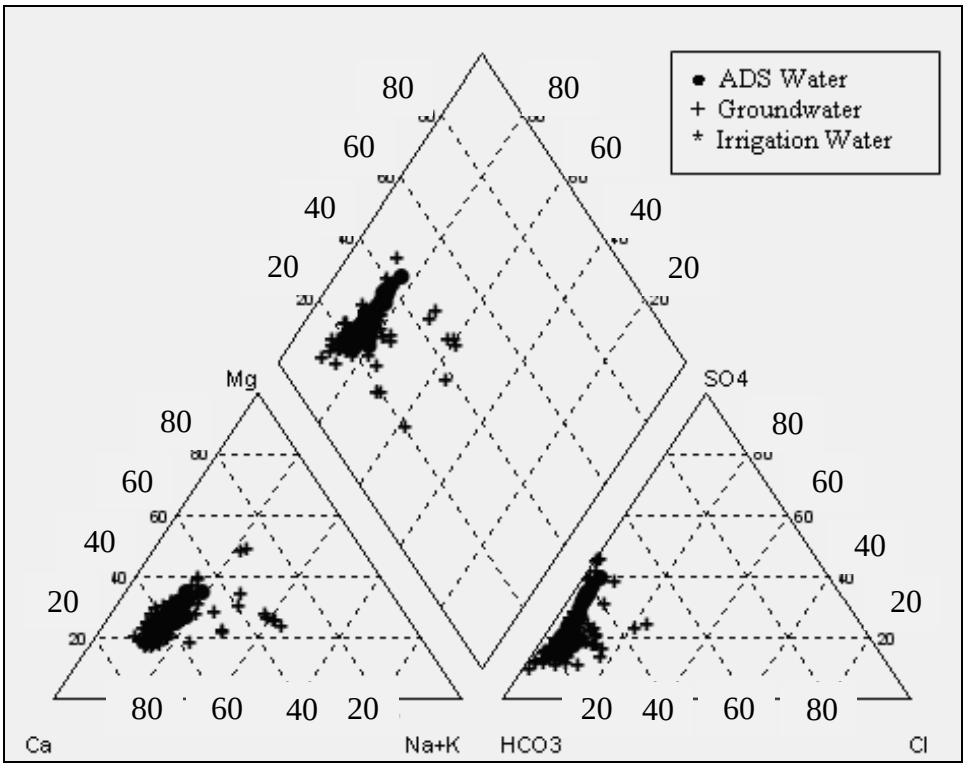

Figure 6.8. Piper diagram showing the chemical composition of agricultural drainage waters, along with groundwaters and irrigation supply water, plotted on the basis of the percent of each ion. Agricultural drainage plots in the same region as groundwaters and irrigation supply water.

fall were likely due to increased irrigation, which resulted in dilution of the agricultural drainage system water and a subsequent decrease in NO_3-N concentrations. Note, however, that the lowest NO_3-N concentrations were measured on January 22, 2007 at OF2 (1.4 mg/l) and EC (1.5 mg/l) following 10 consecutive days (January 6-15, 2007) of temperatures ranging from 1.5 to 10°C (EC, October 2008). Dilution by snow-melt appears to be the most plausible reason for the sharp decrease in NO_3-N concentrations; however, δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values for the January 22, 2007 samples do not support mixing with ^2H- and ^{18}O-depleted values typical of snow. The NO_3-N concentrations measured on January 22, 2007 may have been a result of analytical or sampling error. Mineralization of excess fertilizer N in soils during the spring/summer would, under normal conditions, undergo nitrification to NO_3 in soils over the

summer/fall, and possibly early winter. This would result in high NO_3 concentrations in groundwater over the summer/fall, and possibly early winter. However, because of irrigation with NO_3-poor irrigation waters, NO_3-N concentrations were diluted over the summer/fall, resulting in low NO_3-N concentrations. NO_3 concentrations would be expected to decrease over the winter/spring, as lower temperatures would reduce the rate of nitrification. Instead, the higher NO_3-N concentrations observed over the winter/spring were a result of minimal alteration by dilution.

Historical NO_3-N concentrations at EC decreased 3-fold from 18.3 mg/l in 1997 to an average of 5.7 mg/l in 2000 (Table D.3 of Appendix D), then remained relatively consistent to 2008, with a slight increase at the beginning of 2008 (Figure 6.9). The higher NO_3-N concentrations at EC between 1997 and 2000 were likely due to the more prevalent use of fertilizers.

NO_3-N concentrations measured at 148th also decreased in the summer/early fall and increased in the winter/spring, however, the variation in concentrations was not as large as that measured at OF2 and EC (Figure 6.9). A short-term increase in NO_3-N concentrations was observed at 148th between June and August 2007. During the sampling period, 148th mostly collected groundwater seepage from a nearby orchard that was being converted into a vineyard. By the summer of 2007, the orchard had been removed and grapes planted. The short-term increase may indicate nitrification of fertilizer N initially applied to the new vineyard. NO_3-N concentrations at PH, PHN and PHS were measured during a short period between August and October 2006 and could not be evaluated for trends in the data.

NO_3-N concentrations at PH, PHN and PHS were amongst the highest of all agricultural drainage system waters, indicative of collection of agricultural drainage near the head of the agricultural drainage systems.

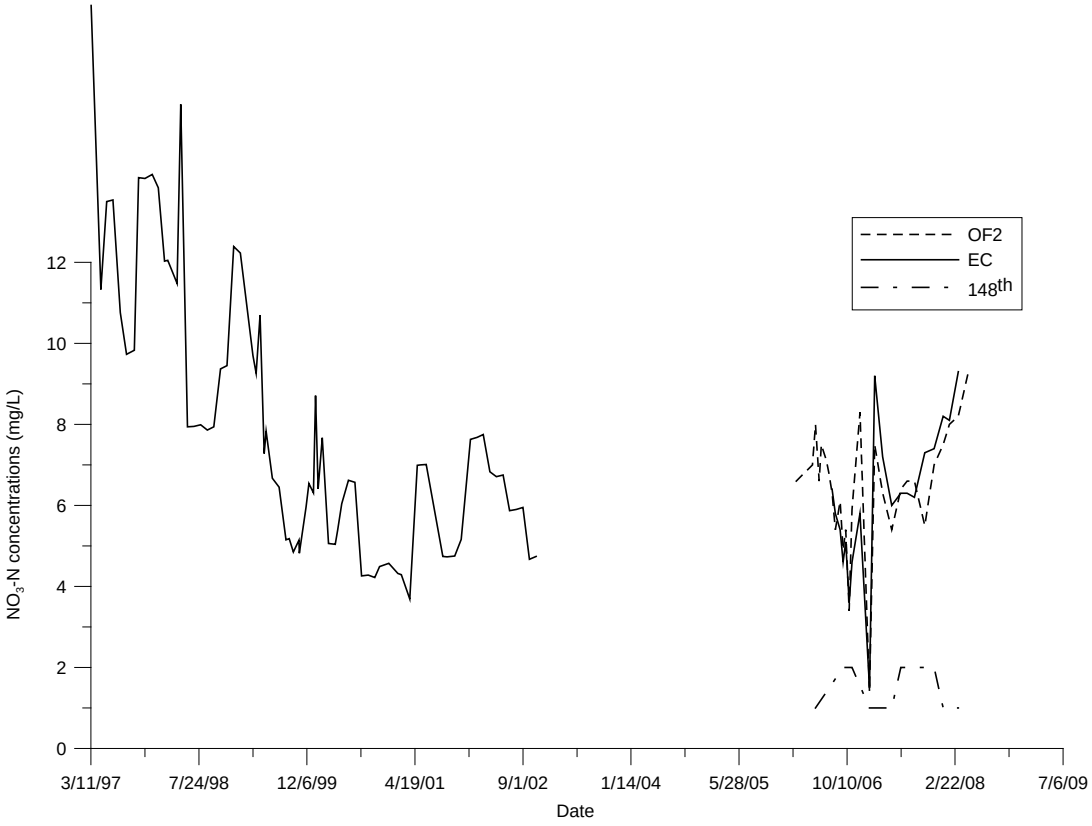

Figure 6.9. NO_3-N concentrations measured at OF2, EC and 148th along ADS O2. NO_3-N concentrations measured at EC between 1997 and 2008 decreased 3-fold from 1997 to 2000, then remained relatively consistent to 2008, with a slight increase at the beginning of 2008.

6.5.2.3.2 ADS O3

NO_3-N concentrations along ADS O3 ranged from 1.0 to 9.5 mg/l (mean of 5.3 ± 2.1 mg/l) at the discharge point into Osoyoos Lake (i.e., OF3), and 2.2 to 4.7 mg/l (mean of 3.6 ± 0.8 mg/l) at Hwy. Groundwater, surface water, and highway storm water all drained into ADS O3, and a small stagnant pond was located immediately up-gradient of the discharge point into Osoyoos Lake. NO_3-N concentrations at OF3 generally increased over the summer/early fall and decreased over the winter/spring (Figure 6.10). The decrease in NO_3-N concentrations at

OF3 did not occur during the summer/early fall, as in OF2. Instead, NO_3-N concentrations at OF3 were more consistent with seasonal nitrification patterns and not a result of dilution by irrigation water. A sharp decrease in NO_3-N was observed at OF3 between May and August 2006, corresponding to the construction of the small pond. NO_3-N concentrations at Hwy decreased over the early fall of 2006 and increased during the remainder of the sampling period (Figure 6.10). The variable trends in NO_3-N concentrations at OF3 and Hwy, and the statistical difference in the medians of the NO_3-N concentrations between locations OF3 and Hwy, were likely a result of multiple drainage sources along ADS O3.

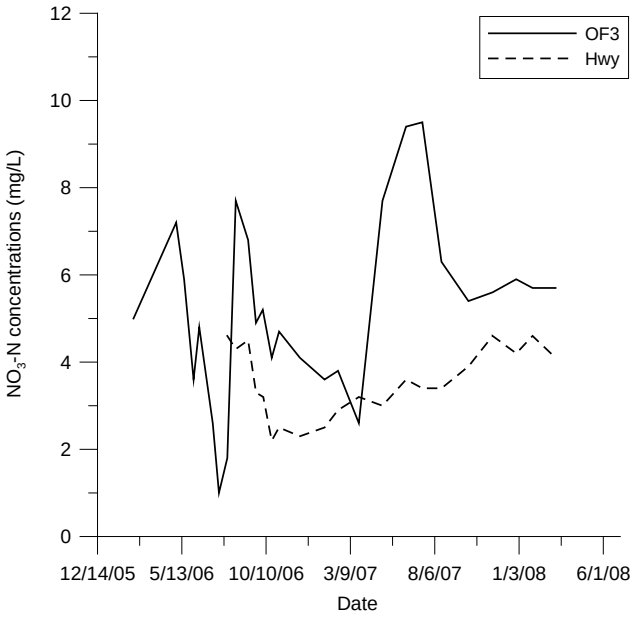

Figure 6.10. NO_3-N concentrations measured at OF3 and Hwy along ADS O3. Variable trends in NO_3-N concentrations represent multiple drainage sources along ADS O3.

6.5.2.4 Isotopes of Water

The δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values of waters collected along ADS O2 and ADS O3 between February 2006 and April 2008 are presented in Table D.3 of Appendix D, and plotted on a δ^2H-$\delta^{18}O$ diagram along with δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values of groundwaters and irrigation

waters collected at the study area (Figure 6.11). δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values of waters along ADS O2 ranged from -107 to -95 ‰ (mean of -102 ± 3‰) and -13.3 to -7.8‰ (mean of -11.5 ± 0.8‰), respectively, at OF2; -109 to -99 ‰ (mean of -102 ± 3‰) and -12.1 to -10.5‰

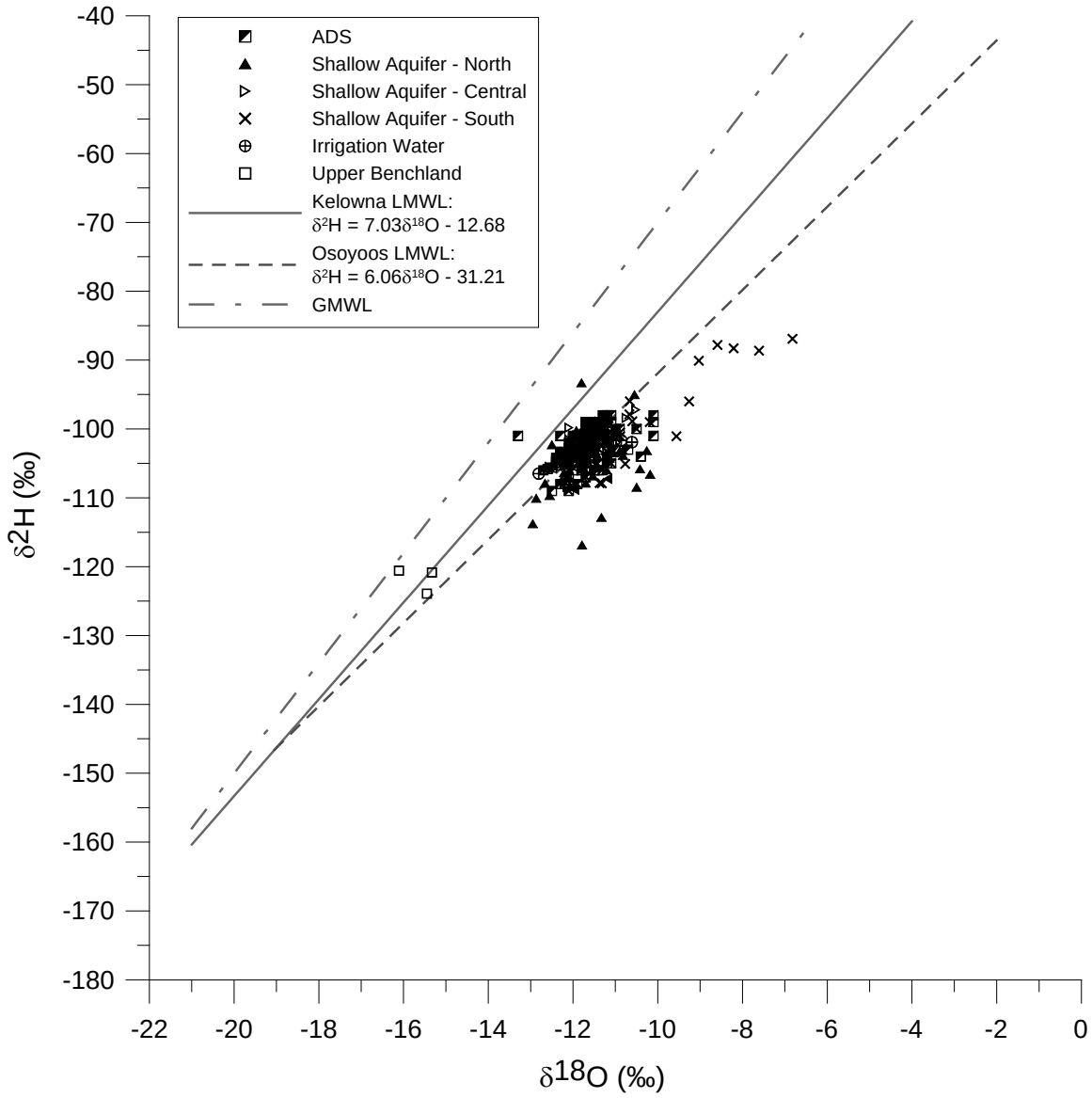

Figure 6.11. δ^2H-$\delta^{18}O$ diagram of agricultural drainage system waters collected between 2006 and 2008, plotted relative to the LMWL for Osoyoos, British Columbia, Canada. Also shown are δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values of shallow groundwaters and irrigation waters from the study area. The LMWL for Kelowna and the GMWL are shown for reference. The δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values of agricultural drainage system waters plot in a similar region as δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values of surrounding shallow groundwaters and their irrigation recharge source.

(mean of -11.6 ± 0.4‰), respectively, at EC; -109 to -100 ‰ (mean of -102 ± 3‰) and -12.5 to -10.4‰ (mean of -11.6 ± 0.4‰), respectively, at 148th; and -106 to -100 ‰ (mean of -104 ± 2‰) and -11.8 to -11.2‰ (mean of -11.5 ± 0.2‰), respectively, at PH, PHN and PHS. δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values of waters along ADS O3 ranged from -108 to -92‰ (mean of -101 ± 3‰) and -12.7 to -9.7 (mean of -11.3 ± 0.7‰), respectively, at OF3; and -106 to -98‰ (mean of -101 ± 2‰) and -12.0 to -10.1 (mean of -11.3 ± 0.4‰), respectively, at Hwy. δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values of waters along ADS O2 and ADS O3 plot in a similar range as δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values of surrounding shallow groundwaters and their predominant recharge source (irrigation water), confirming that both ADS O2 and ADS O3 drained the surrounding shallow groundwaters.

The δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values of waters collected at EC between March 1997 and November 2002 are presented in Table D.3 of Appendix D, and plotted on a separate δ^2H-$\delta^{18}O$ diagram (Figure 6.12). δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values ranged from -106 to -101‰ (mean of -104 ± 1‰) and -12.6 to -11.6 ‰ (mean of -12.1 ± 0.3‰), respectively. A positive correlation existed between δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values, where values became more positive (evaporitic) over time ($\Delta_{\delta 2HH2O} \approx 4‰$ and $\Delta_{\delta 18OH2O} \approx 1.0‰$). Linear regression of the δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values produced a line with the equation $\delta^2H = 3.98\ \delta^{18}O - 55.5$. The δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values of waters at EC between August 2006 and April 2008 were generally up to 7‰ and up to1.4‰, respectively, more positive than the 1997-2002 samples (Figure 6.12). In fact, δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values of waters collected at all locations along ADS O2 were generally more positive than the 1997-2002 samples. The data suggest that large scale evaporation of Osoyoos Lake, and, accordingly, the Okanagan River system, occurred since at least 1997.

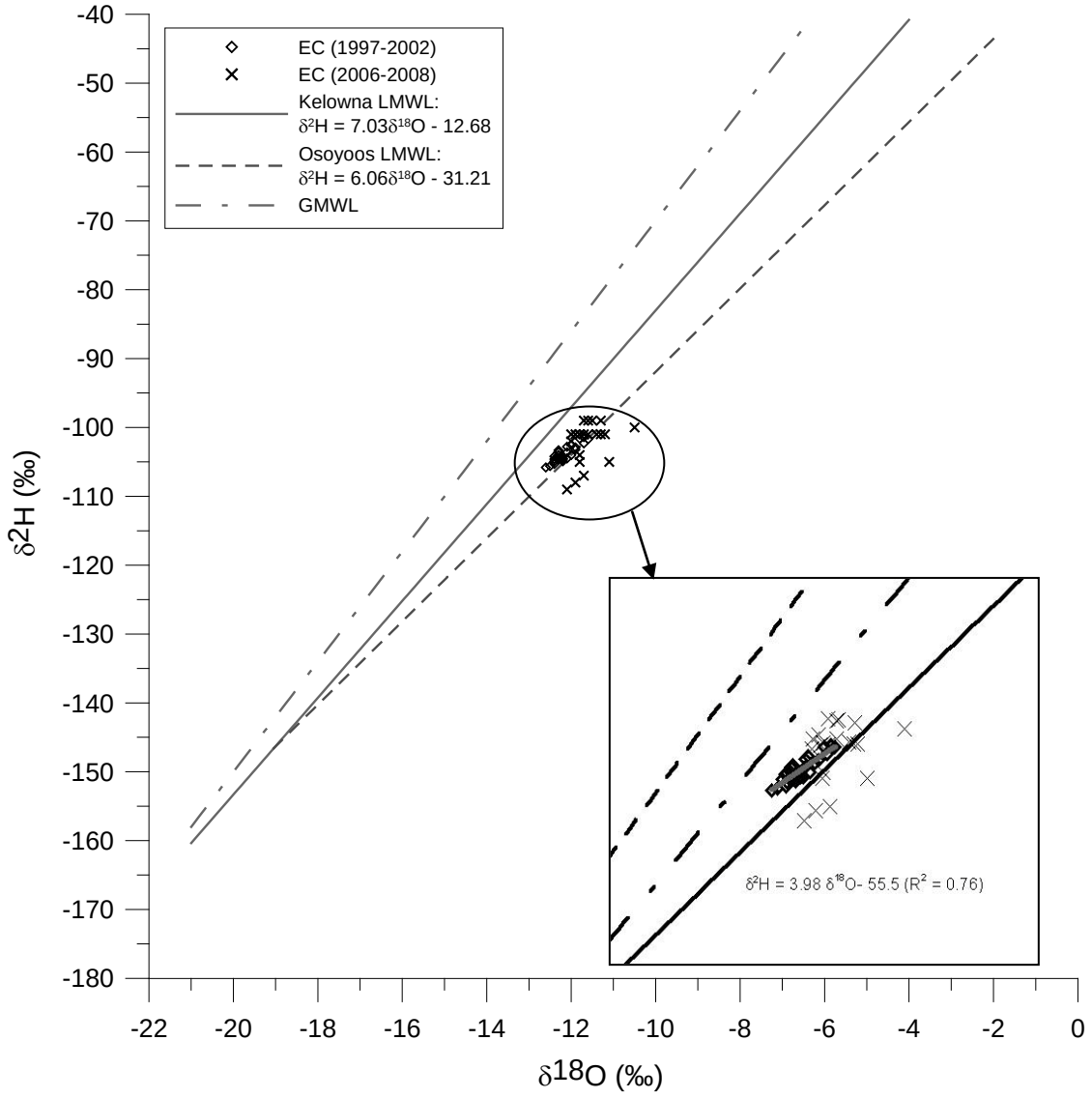

Figure 6.12. δ^2H-$\delta^{18}O$ diagram showing δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values of agricultural drainage system waters collected at EC between 1997 and 2008, plotted relative to the LMWL for Osoyoos, British Columbia, Canada. The LMWL for Kelowna and the GMWL are shown for reference. The inset provides a closer view of the δ^2H-$\delta^{18}O$ relationship, where δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values from 1997 to 2002 become more positive (evaporitic) over time.

6.5.2.5 Isotopes of NO_3

$\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ values of waters collected along ADS O2 and ADS O3 between March 1997 and April 2008 are presented in Table D.3 of Appendix D and plotted on a $\delta^{15}N$-$\delta^{18}O$ diagram (Figure 6.13). Also included on Figure 6.13 are (1) the range in $\delta^{15}N$ values

of synthetic fertilizers used in the study area; (2) the range in $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ values for the various other sources of NO_3; (3) the range in calculated $\delta^{18}O_{NO3}$ values for groundwaters in the study area; and (4) $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ values for groundwaters collected in the study area between February 2006 and February 2007.

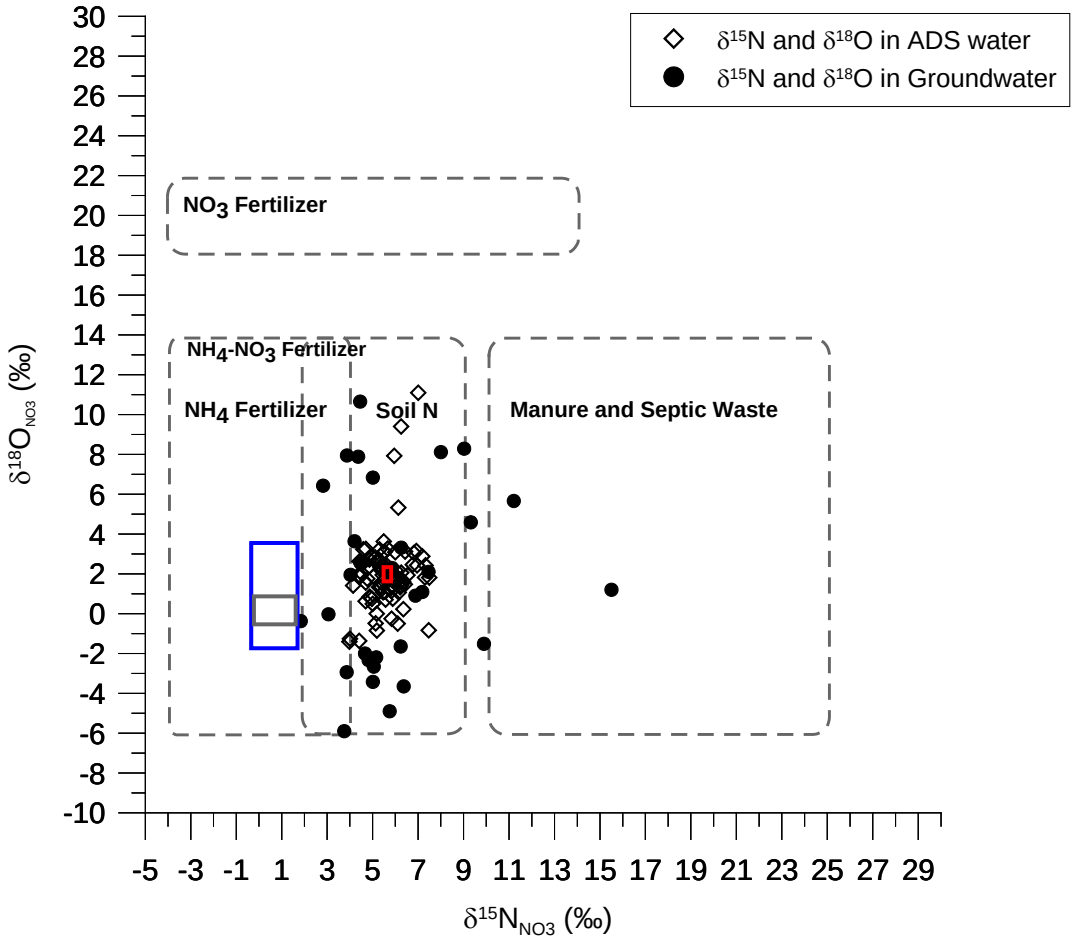

Figure 6.13. $\delta^{15}N$-$\delta^{18}O$ crossplot showing $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ values of agricultural drainage system waters in the study area. Also shown are $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ values of groundwaters in the study area. The red box represents the 95% CI of the sampling mean for $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ values of agricultural drainage system waters. Dashed lines represent literature $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ ranges for the various NO_3 sources. The blue rectangle represents the range in $\delta^{15}N$ values of synthetic fertilizers used in the study area and the range in calculated $\delta^{18}O_{NO3}$ values for groundwaters in the study area. Within the blue rectangle, the grey rectangle represents the 95% CI of the sampling means for the $\delta^{15}N$ and predicted $\delta^{18}O_{NO3}$ values.

6.5.2.5.1 $\delta^{15}N_{NO3}$

$\delta^{15}N_{NO3}$ values of waters collected along ADS O2 ranged from +4.0 to +7.2 ‰ (mean of +5.6 ± 1.4‰). $\delta^{15}N_{NO3}$ values of waters collected along ADS O3 ranged from +6.0 to +7.0 ‰ (mean of +6.3 ± 0.4‰). $\delta^{15}N_{NO3}$ values of waters collected along ADS O2 and ADS O3 plot within the range of groundwater $\delta^{15}N_{NO3}$ values, indicative of NO_3 in groundwater traveling and entering agricultural drainage systems in a conservative manner with no to minimal isotopic fractionation of N (*i.e.*, denitrification).

$\delta^{15}N_{NO3}$ values in agricultural drainage system waters collected at EC between 1997 and 2002 are shown on Figure 6.14, along with NO_3-N concentrations measured at EC during this period. $\delta^{18}O_{NO3}$ values are also shown on Figure 6.14, however, they are discussed in more detail in Section 6.5.2.5.2. An annual or seasonal trend in $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ values was not identified. Between each of the 74 sampling events (n = 73 intervals), $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ values increased or decreased simultaneously approximately 60% of the time. The remaining 40% of the time, $\delta^{15}N_{NO3}$ values increased while $\delta^{18}O_{NO3}$ values decreased (or vice versa). Where trends in $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ values were similar, NO_3-N concentrations appeared to follow the same trend approximately 60% of the time (*i.e.*, $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ values and NO_3-N concentrations increased or decreased simultaneously). Where $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ values showed opposing trends, NO_3-N concentrations appeared to follow the trend in $\delta^{18}O_{NO3}$ values approximately 75% of the time (*i.e.*, $\delta^{18}O_{NO3}$ values and NO_3-N concentrations increased or decreased simultaneously). Based on the variable nature of $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ values and NO_3-N concentrations in agricultural drainage waters at EC between 1997 and 2002, it was not

possible to confirm what, if any, isotopic fractionation processes were occurring (see Section 6.5.2.5.2).

Between October 1999 and April 2001, $\delta^{15}N_{NO3}$ values increased by roughly 2.2‰. The cause of the increase could not be determined with the available data. Since the increase in $\delta^{15}N_{NO3}$ values occurred during the winter/spring, it could not be explained by N isotope fractionation during nitrification, as nitrification rates are generally lowest during this time of

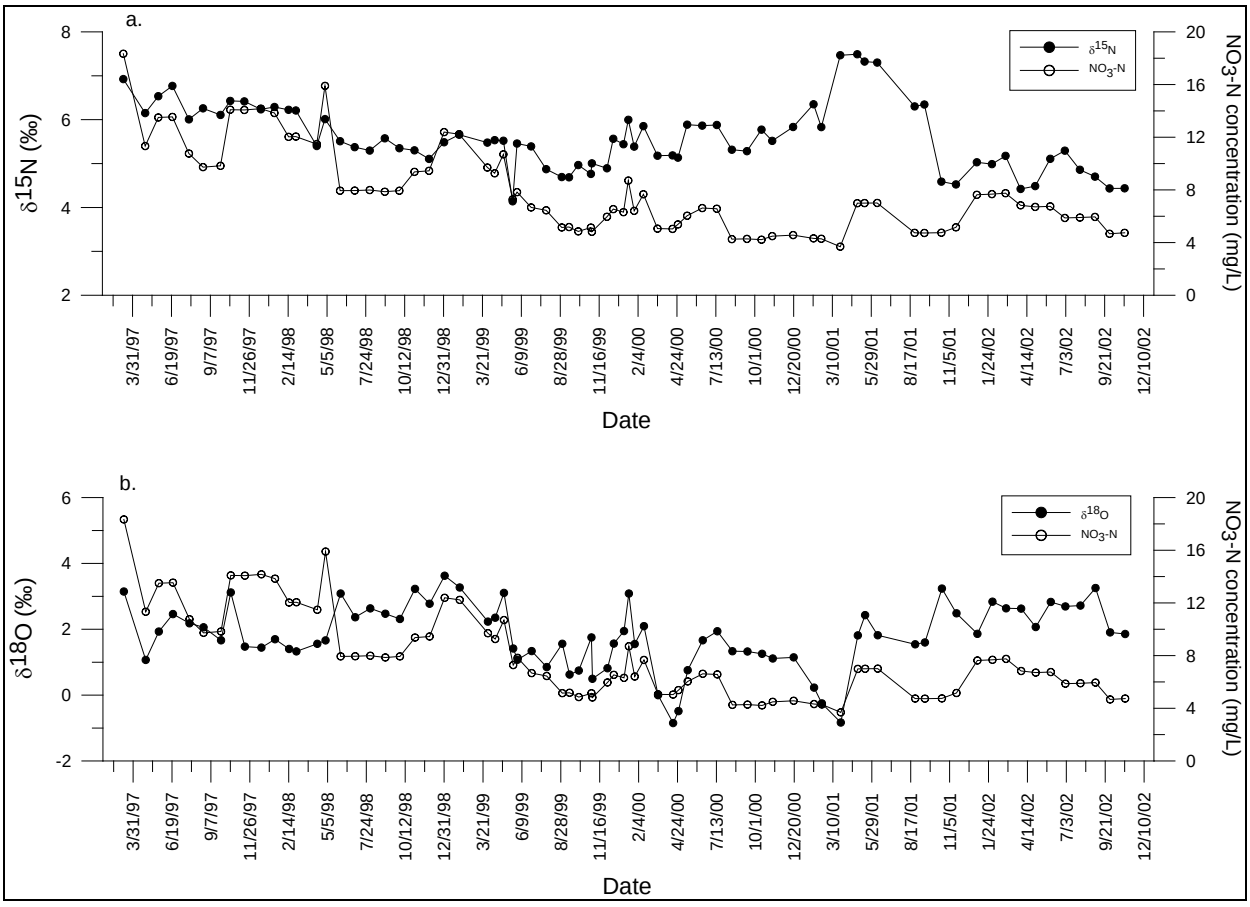

Figure 6.14. a. $\delta^{15}N_{NO3}$ values of agricultural drainage system waters collected at EC between 1997 and 2002. b. $\delta^{18}O_{NO3}$ values of agricultural drainage system waters collected at EC between 1997 and 2002. NO_3-N concentrations of agricultural drainage system waters collected at EC during this time period are provided on each figure on the right-hand axis.

year, nor by mixing of nitrified NO_3 from ammoniacal fertilizer N with NO_3 originating from NO_3 fertilizer and/or NH_4-NO_3 fertilizer (Karr et al., 2001). Denitrification was also ruled out as a cause of the increase, as a corresponding increase in $\delta^{18}O_{NO3}$ values was not observed. Kellman and Hillaire-Marcel (2003) showed that increasing $\delta^{15}N_{NO3}$ values in tile drainage waters at the Prescott site were predominantly a result of denitrification. At the Prescott site, increasing $\delta^{15}N$ values and decreasing NO_3 concentrations were repeatedly observed following storm events, suggesting that soil NO_3 mobilized by precipitation events was undergoing denitrification during its subsequent transport to tile drains (Kellman and Hillaire-Marcel, 2003). At EC, increases in $\delta^{15}N_{NO3}$ values (with corresponding increases in $\delta^{18}O_{NO3}$ values) could not be explained by denitrification.

Denitrification is represented as the inverse relationship between $\delta^{15}N_{NO3}$ values and NO_3 concentrations, where $\delta^{15}N_{NO3}$ values are plotted against the natural logarithm of NO_3 concentrations (Kendall, 1998). A positive relationship, not an inverse relationship, was observed between $\delta^{15}N_{NO3}$ values and the natural logarithm of NO_3-N concentrations of waters at EC (Figure 6.15), confirming that denitrification had not taken place. Mixing of fertilizer and septic/manure NO_3 sources is represented as a positive correlation between $\delta^{15}N_{NO3}$ values and NO_3 concentrations, where $\delta^{15}N_{NO3}$ values are plotted against $1/NO_3$ concentrations (Kendall, 1998). A positive correlation was not observed between $\delta^{15}N_{NO3}$ values and $1/NO_3$-N concentrations of waters at EC (Figure 6.15), confirming that mixing of fertilizer NO_3 and septic/manure NO_3 had not taken place.

6.5.2.5.2 $\delta^{18}O_{NO3}$

$\delta^{18}O_{NO3}$ values of water samples collected along ADS O2 ranged from -1.4 to +3.0‰ (mean of +0.8 ± 1.9‰). $\delta^{18}O_{NO3}$ values of water samples collected along ADS O3 ranged from

-0.5 to +11.1‰ (mean of +5.8 ± 4.6 ‰). $\delta^{18}O_{NO3}$ values of water samples collected along ADS O3 were more variable than $\delta^{18}O_{NO3}$ values of samples collected along ADS O2. All $\delta^{18}O_{NO3}$ values were less than those of NO_3 and/or NH_4-NO_3 fertilizers and consistent with NO_3 originating from nitrification of reduced forms of fertilizer N (*i.e.*, NH_4), with the exception of

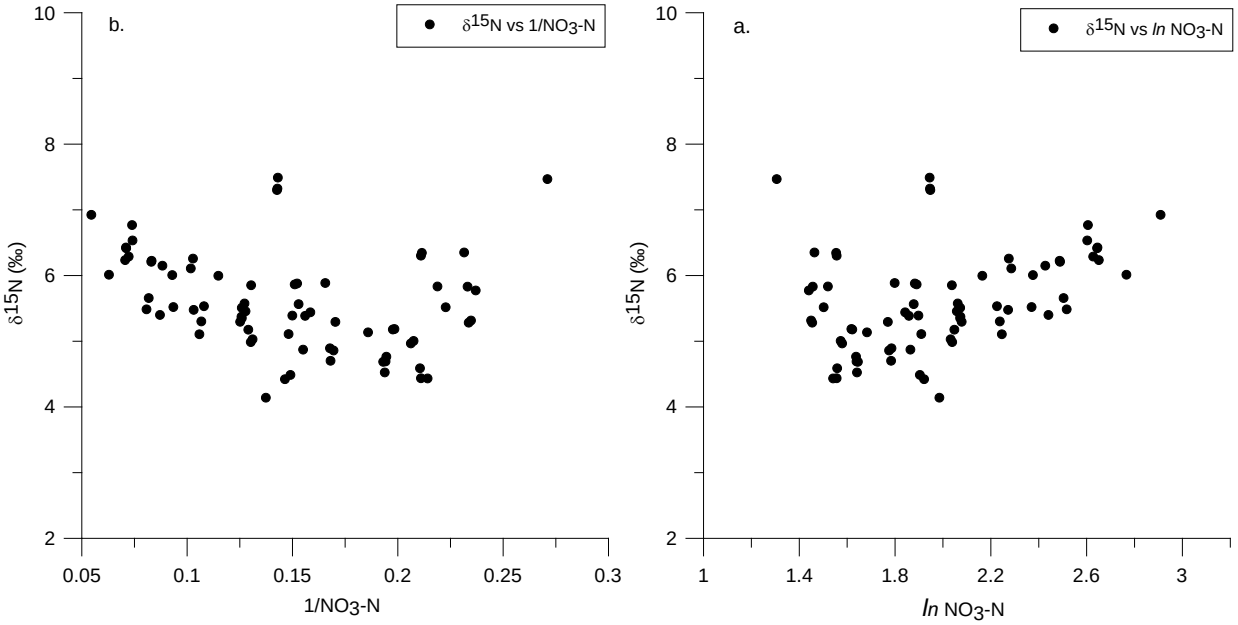

Figure 6.15. a. $\delta^{15}N_{NO3}$ values vs. natural logarithm of NO_3-N concentrations of waters collected at EC between 1997 and 2002, as an indicator of denitrification. b. $\delta^{15}N_{NO3}$ values vs. 1/NO_3-N concentrations of waters collected at EC between 1997 and 2002, as an indicator of mixing of fertilizer NO_3 and septic/manure NO_3.

four water samples collected at OF3, where $\delta^{18}O_{NO3}$ values ranged from +5.3 to +11.1‰. The four water samples with the highest $\delta^{18}O_{NO3}$ values were indicative of mixing of nitrified NO_3 from ammoniacal fertilizer N with NO_3 originating from NO_3 fertilizer and/or NH_4-NO_3 fertilizer (Karr et al., 2001). The higher $\delta^{18}O_{NO3}$ values were not indicative of denitrification of NO_3 derived from synthetic fertilizers, as an increase in $\delta^{15}N_{NO3}$ values was not accompanied by an increase in $\delta^{18}O_{NO3}$ values, even during the period corresponding to the construction of the small pond immediately up-gradient of OF3. The NO_3-N concentration measured in agricultural drainage at OF3 on May 17, 2006 (5.9 mg/l) decreased to 1.0 mg/l on July 18, 2006. However,

the increase in $\delta^{15}N_{NO3}$ values of +6.3‰ (May) and +7.0‰ (July) and $\delta^{18}O_{NO3}$ values of +9.4‰ (May) and +11.1‰ (July) occurred at a much lower ratio than the 2:1 enrichment in $^{15}N_{NO3}$ and $^{18}O_{NO3}$, respectively, observed for denitrification. Additionally, although high iron and manganese concentrations suggest that reducing conditions in the pond were favourable for denitrification, decreasing alkalinity and sulphate concentrations between May and August 2006 did not support denitrification. Denitrification and other reduction reactions that consume acidity are typically associated with increases in alkalinity (as bicarbonate) resulting from oxidation of organic matter and/or increases in sulphate resulting from oxidation of iron sulphides (Bohlke, 2002; Kendall, 1998).

Continuous $\delta^{18}O_{NO3}$ values in agricultural drainage system waters collected at EC between 1997 and 2002 are shown on Figure 6.14. As stated earlier, isotopic fractionation processes in agricultural drainage waters at EC between 1997 and 2002 could not be absolutely confirmed (except that denitrification had not occurred). Where decreasing $\delta^{15}N_{NO3}$ values were accompanied by increasing $\delta^{18}O_{NO3}$ values and NO_3-N concentrations, N isotope fractionation during nitrification may have resulted in a decrease in $\delta^{15}N_{NO3}$ values due to increased nitrification rates and the increased N isotope fractionation that occurs during nitrification (Kendall, 1998). Increasing $\delta^{15}N_{NO3}$ values may have been indicative of a decrease in the nitrification rate (Kendall, 1998). Increasing or decreasing $\delta^{18}O_{NO3}$ values may have been a result of variable proportions of oxygen sources involved in nitrification (Aravena et al., 1993; Mayer et al., 2001) and/or that residual recharge and soil waters having higher $\delta^{18}O$ values due to evaporative enrichment were involved in the nitrification process (Wassenaar, 1995). Deutsch et al. (2006) showed that an increase in $\delta^{18}O_{NO3}$ in an agricultural tile drain at the Warnow River site was accompanied by a decrease in $\delta^{15}N_{NO3}$ and NO_3 as a result of a snowmelt event a few

days before sampling. At the Warnow River site, the soil water mixed with NO_3-poor snowmelt water having typically high $\delta^{18}O_{NO3}$ values (> 30‰) and low $\delta^{15}N_{NO3}$ values (Deutsch et al., 2006). Snowmelt and rainwater at the study area were not analyzed for $\delta^{18}O_{NO3}$ and $\delta^{15}N_{NO3}$ values, and therefore, their affect, if any, on the isotopic composition of agricultural drainage waters is not known. However, as $\delta^{18}O_{NO3}$ values measured at EC were less than 3.6‰, it is unlikely that direct snowmelt and/or rainwater had much of an affect on the isotopic composition of the agricultural drainage waters.

6.6 Summary and Conclusions

The source of elevated and widespread NO_3-N concentrations in groundwaters and agricultural drainage in the Osoyoos area was quantified using physical and chemical parameters, stable isotopes of NO_3 ($^{15}N_{NO3}$ and $^{18}O_{NO3}$), stable isotopes of waters ($^{2}H_{H2O}$ and $^{18}O_{H2O}$) and stable isotopes of dissolved oxygen in waters ($^{18}O_{DO}$). Groundwaters and agricultural drainage were contaminated by inorganic fertilizer N applied at the soil surface. Volatilization of NH_3 from fertilizer N applied as either urea, urea in blended fertilizers, or (historically) NH_4-NO_3, occurred between fertilizer N application at the beginning of March and commencement of irrigation in mid-April. Volatilization of NH_3 raised the $\delta^{15}N$ values from -0.4 to +1.7‰ to within +1.8 to +7.5‰, or roughly up by +7.9‰. Following nitrification of residual N not taken up by trees/vines, newly-formed NO_3 was advanced into the saturated zone via irrigation. Seven groundwater samples and four agricultural drainage samples exhibited comparatively higher $\delta^{18}O_{NO3}$ values than all other $\delta^{18}O_{NO3}$ values. The samples with higher $\delta^{18}O_{NO3}$ values were indicative of mixing of NO_3 from ammoniacal fertilizer N with NO_3 originating from NO_3 fertilizer and/or NH_4-NO_3 fertilizer. Only six groundwater samples exhibited higher $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ values, and coupled with low DO and Cl concentrations,

were suggestive of localized denitrification. NO_3 in groundwaters and agricultural drainage was not derived from septic or manure sources, nor from mixing of fertilizer N and septic/manure N. Conditions in the unsaturated zone and in groundwaters in the study area were generally not favourable for natural remediation by denitrification.

NO_3-N concentrations in 50% of the groundwaters sampled exhibited a decreasing trend over time. NO_3-N concentrations in agricultural drainage decreased 3-fold between 1997 and 2008. The decrease in NO_3-N concentrations likely reflects a positive shift in improved fertilizer use and management in the study area, or, possibly, the affect of the onset of emerging vineyards which use significantly lower amounts of fertilizer N and irrigation water.

Shallow groundwaters, predominantly recharged by irrigation, were collected in agricultural drainage systems and discharged directly into Osoyoos Lake. Discharge rates generally corresponded to the irrigation cycle, where rates increased over the summer/early fall and decreased over the winter/spring. NO_3-N concentrations in agricultural drainage were significantly influenced by the application of irrigation water. Irrigation with NO_3-poor irrigation waters over the summer/fall resulted in lower (diluted) NO_3-N concentrations. The higher NO_3 concentrations observed over the winter/spring were a result of minimal alteration by dilution. $\delta^{15}N_{NO3}$ values of waters collected in agricultural drainage were indicative of NO_3 in groundwater traveling and entering agricultural drainage systems in a conservative manner with no to minimal isotopic fractionation of N (*i.e.*, denitrification).

6.7 Acknowledgements

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CHAPTER 7
CONCLUSIONS, IMPLICATIONS AND RECOMMENDATIONS

7.1 Conclusions

This thesis demonstrates that stable isotope analysis, when combined with geochemistry, age dating, and physical hydrogeological methods, can be an effective means of characterizing the hydrogeology of a region and contaminant sources affecting regional water supplies. For this M.Sc. study, (1) stable isotopes of water, nitrate and dissolved oxygen, (2) tritium, tritium/helium and radiocarbon age dates, (3) geochemical parameters, and (4) water levels were measured from different water sources (precipitation, surface waters, groundwaters and agricultural drainage waters) extending from the Okanagan valley bottom to the highlands. The results were used to successfully characterize the regional hydrogeological setting of the South Okanagan Basin and to confirm contaminant nitrate sources in shallow groundwaters in the Osoyoos area.

The South Okanagan Basin is the driest and warmest region of the Basin. High evapotranspiration rates give rise to water deficits during the summer months and a consequential dependency on irrigation water for agricultural productivity. As such, surface waters of the Okanagan River and Osoyoos Lake are used as irrigation sources in the South Okanagan Basin valley and irrigation return flow has become the primary source of recharge for shallow groundwaters. Bedrock fractures in the highlands east and west of the South Okanagan Basin valley do not appear to be significant recharge sources for these shallow groundwaters.

The lack of major creeks and tributaries discharging into the Okanagan River system in the South Okanagan Basin (with the exception of Inkameep Creek northeast of Osoyoos), and consequently the lack of alluvial fan deposits at the base of these creeks and tributaries, further precludes the movement of surface water and groundwater from the highlands to the valley. Thus, precipitation falling in the highland areas appears to be transported deep into bedrock fractures and may move as groundwater below the South Okanagan Basin valley deposits. As irrigation return flow controls the shallow groundwater dynamics in the South Okanagan Basin valley, groundwater quality is susceptible to contamination by human activities. In the Osoyoos valley, elevated levels of nitrate are present in shallow groundwaters as a result of fertilizer nitrogen applied mostly at orchards. Agricultural drainage systems in the north part of Osoyoos discharge groundwater directly into Osoyoos Lake and may be contributing to its eutrophication. Note that the water quality of the Okanagan River up-gradient of Osoyoos Lake is also affected by human activities, and potential impacts by nitrate (and other parameters, for example, phosphorous) in the Okanagan River up-gradient of Osoyoos Lake may also be contributing to eutrophication of Osoyoos Lake.

7.2 Implications and Recommendations for Further Work

Implications of this research and/or recommendations for further work are provided for each chapter of this M.Sc. thesis.

7.2.1 Precipitation in the Okanagan Basin - Refining the LMWLs of the Basin

Statistical analysis of the slope and intercept of the LMWLs for Kelowna and Osoyoos showed that there was no correlation between the δ^2H-$\delta^{18}O$ relationship of precipitation falling in Osoyoos with that of precipitation falling in Kelowna. This suggests that spatial and/or temporal variations in the isotopic composition of precipitation falling in the Okanagan Basin

exist from the central part of the Basin (*i.e.*, Kelowna) to the south. The addition of at least one more precipitation sampling station in the north part of the Okanagan Basin (*i.e.*, Vernon) would provide more detailed information on these spatial and/or temporal variations throughout the Okanagan Basin.

Amount-weighted δ^2H and $\delta^{18}O$ values of precipitation provided in this M.Sc. thesis were estimated, as the amount of precipitation falling in the immediate vicinity of precipitation collectors could not logistically be measured. Note, these amount-weighted δ^2H and $\delta^{18}O$ values are considered to be acceptable as precipitation collection stations were located within 5 km of the nearest Environment Canada weather station. Future research involving isotopic analysis of precipitation in the Okanagan Basin should involve collection of precipitation samples in close proximity to established weather stations where precipitation amounts are consistently measured. Provided that samples are collected over a minimum period of two years, this approach would generate a more precise LMWL for a given region within the Okanagan Basin.

7.2.2 Surface Waters of the Okanagan River System - Additional Assessments

Conclusions made in this M.Sc. thesis regarding the dynamics of the Okanagan River system, including Okanagan Lake and Osoyoos Lake, are preliminary. In order to better understand the dynamics of the lakes comprising the Okanagan River system (including lake mixing, residence times and recharge sources), all surface water and groundwater inputs and outputs would need to be quantified and isotopic and geochemical depth profiles of each lake would be necessary. Additionally, a better understanding of the interaction between highland catchment areas and the Okanagan River system above the outlet of Okanagan Lake is needed. The average evaporative loss and evaporation-to-inflow ratio calculated for the fraction of water loss by evaporation in the Okanagan River system was estimated based on available isotopic data

and the assumption that evaporation of surface waters within the Okanagan River system took place within watershed tributaries and creeks and during storage in the system. The fraction of water loss by evaporation in the Okanagan River system should be confirmed using other methods.

7.2.3 Exclusivity of Regional Hydrogeological Model of the South Okanagan Basin

Conclusions made in this M.Sc. thesis regarding the regional hydrogeological setting of the South Okanagan Basin are specific to this region of the Basin. Although a similar multi-faceted approach can be used to assess other parts of the Okanagan Basin, recharge environments may not be identical. For example, irrigation return flow may not play as significant a role in shallow groundwater recharge in other regions of the Okanagan Basin as it does in the South Okanagan Basin valley. Additionally, in the north and central parts of the Okanagan Basin where precipitation is greater, temperatures are slightly cooler and evapotranspiration rates are lower, precipitation may be a more significant recharge source for groundwater aquifers in the valley. Furthermore, highland catchment areas may act as substantially greater recharge sources for surface waters and groundwaters in the valley, especially in areas where large alluvial fans associated with major creeks and tributaries discharging into the Okanagan River system are present.

7.2.4 Improving Shallow Groundwater Quality in the Osoyoos Area due to Nitrate Contamination from Fertilizer Sources

With respect to farming practices in the Okanagan Basin (including the Osoyoos area), it is well known that two critical issues requiring action by municipal, provincial and federal agencies, and by individual farmers themselves, are: (1) protection of groundwater and surface water resources from adverse affects due to application of agricultural chemicals, and (2) irrigation management practices. The Canada-British Columbia Environmental Farm Plan

Program, a partnership between Agriculture and Agri-food Canada, the British Columbia Ministry of Agriculture and Lands, and the British Columbia Agriculture Council, is a valuable resource for information on agricultural best management practices and whose mandate includes assurance of the "*future of the BC agricultural industry through the further implementation of Beneficial Management Practices*" (British Columbia Agriculture Council, January 2008). Numerous internet resources and documents on irrigation practices are available to assists farmers and managers in improving water management and implementing beneficial irrigation management practices (British Columbia Ministry of Agriculture and Lands Resource Management [January 2008]; Irrigation Industry Association of British Columbia [January 2008]). Additional information regarding agricultural best management practices and water management is available from the waterbucket website (www.waterbucket.ca) and the Farmwest website (www.farmwest.com). With the considerable amount of information available to enable farmers and managers to implement better agriculture practices, it is troubling that elevated nitrate concentrations still exist in shallow groundwaters in the South Okanagan Basin. One explanation for nitrate's persistence may be that the source of nitrate in shallow groundwater has never been confirmed. This M.Sc. thesis identified that the source of nitrate in shallow groundwaters in the Osoyoos area originated from the application of fertilizer nitrogen, and that irrigation exacerbated the transport of nitrate into Osoyoos Lake via agricultural drainage systems. With this knowledge, farmers and managers may be able to apply the appropriate management practices best suited to the storage and/or handling of fertilizer nitrogen and to the subsequent application of irrigation waters. Note that as agricultural best management practices are not regulated by the province, it is left up to the farmer and/or manager to decide whether or not they want, or can afford, to implement these practices.

In conjunction with best management practices, an effective and increasingly popular method of chemically attenuating nitrate concentrations in groundwater and agricultural drainage waters is the construction of denitrification barriers (Blowes et al., 1994; Robertson et al., 2000; Schipper and Vojvodic-Vukovic, 2001; Volokita et al., 1996). These barriers are installed perpendicular to groundwater-agricultural drainage flow in shallow groundwater environments and constructed of permeable, carbonaceous (organic) materials, including wood mulch (Robertson et al., 2000). The organic matter acts as a carbon source to microbial heterotrophic and denitrifying bacteria, where the heterotrophs remove oxygen from the water providing an anaerobic environment, and the denitrifiers use the carbon to convert nitrate in the water to nitrogen gases (Schipper and Vojvodic-Vukovic, 2001). Implementation of denitrification barriers at agricultural drainage systems in the Osoyoos area would prevent nitrate in agricultural drainage systems from entering Osoyoos Lake, thereby lessening the potential for eutrophication (Blowes et al., 1994).

In this study, estimates of NO_3-N loading into Osoyoos Lake from known agricultural drainage systems were provided. It is recommended that NO_3-N loading into Osoyoos Lake from other sources, including the Okanagan River system to the north, and groundwater seepage west and east of Osoyoos Lake, be evaluated to better determine the effect, if any, that these sources of NO_3 have on the eutrophication of Osoyoos Lake.

Lastly, and as a consideration, the reduction of fertilizer nitrogen applied at orchards in the South Okanagan Basin may come about naturally if the current practice of replacing orchards with vineyards continues. Vineyards typically use less fertilizer nitrogen and require less irrigation water, the two issues responsible for the elevated nitrate concentrations in shallow groundwater in the Osoyoos area.

7.3 References

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APPENDIX A
PRECIPITATION DATA

δ^2H and $\delta^{18}O$ values of precipitation collected in the Okanagan Basin, British Columbia, Canada, are provided in Table A.1.

Table A.1. δ^2H, $\delta^{18}O$ and d-excess values for precipitation collected in the Okanagan Basin from April 2006 to April 2008. Climate data (total precipitation [Total pptn], average temperatures [Avg. temp]) are from nearby Environment Canada weather stations for the duration of each sampling interval. Red values discarded as δ^2H_{H2O} or $\delta^{18}O_{H2O}$ may have been affected by evaporation during storage. Shaded sample number indicates samples were collected concurrently from West Osoyoos and West Kelowna to assess potential spatial trends in the isotopic composition of precipitation. Blue values represent estimated precipitation amounts and estimated average temperatures, as the nearby Environment Canada weather station had missing climate data for the respective sampling intervals. Underlined values indicate that precipitation amounts and average temperatures were for estimated sampling intervals.

Station	Sample	Date sampled (m/dd/yy)	δ^2H (‰)	$\delta^{18}O$ (‰)	d-excess (‰)	Total pptn (mm)	Avg. temp (ºC)
Osoyoos	1	4/19/06	-115	-14.4	-0.1	50.3	8.2
West	2	6/2/06	-89	-10.6	-3.8	57.1	15.3
	3	7/7/06	-81	-9.5	-5.5	88.4	20.8
49.05°N,	4	8/2/06	-102	-11.3	-11.8	3.6	23.9
119.52°W	5	9/8/06	-91	-11.2	-1.8	**0.4**	20.7
360 masl	6	10/4/06	**-55**	**-2.6**	**-33.7**	9.2	16.0
	7	11/2/06	-116	-13.1	-11.5	18.8	9.2
	8	12/16/06	-114	-15.6	10.8	87.2	1.7
	9	1/22/07	-150	-19.0	2.8	23.8	-2.6
	10	2/19/07	-144	-18.3	1.7	11.2	1.1
	11	3/24/07	**-68**	**-3.6**	**-38.9**	**18.4**	**6.9**
	12	5/5/07	-113	-13.4	-5.9	**0.6**	**10.3**
	13	6/16/07	**-28**	**6.2**	**-76.8**	33.3	17.3
	14	10/5/07	-75	-6.1	-26.1	**28.5**	**16.8**
	15	11/17/07	**-58**	**-4.0**	**-26.2**	29.1	8.3
	16	12/29/07	-142	-18.9	8.8	**43.2**	**-0.2**
	17	1/27/08	-147	-18.7	2.5	31.2	-3.0
	18	3/8/08	-109	-12.7	-7.2	9.8	1.7
	19	4/24/08	-92	-8.2	-26.4	9.4	7.0
		Minimum	-150	-19.0	-26.4		
		Maximum	-75	-6.1	10.8		
		Average	-112	-13.4	-5.0		
		Std. dev.	25	4.1	11.2		

Table A.1 continued

Station	Sample	Date sampled (m/dd/yy)	δ^2H (‰)	$\delta^{18}O$ (‰)	d-excess (‰)	Total pptn (mm)	Avg. temp (°C)
Osoyoos	1	3/1/06	-157	-18.3	-10.7	32.0	1.7
East	2	4/6/06	-111	-13.7	-1.3	31.9	7.5
	3	6/2/06	-86	-7.5	-25.9	51.5	15.8
49.03°N,	4	6/29/06	-95	-9.6	-18.4	72.1	19.8
119.40°W	5	11/7/06	-85	-9.6	-7.9	22.0	9.4
810 masl	6	12/8/06	-82	-11.5	9.8	44.6	0.3
	7	6/11/07	-115	-13.4	-7.5	31.2	19.2
		Minimum	-157	-18.3	-25.9		
		Maximum	-82	-7.5	9.8		
		Average	-104	-11.9	-8.8		
		Std. dev.	27	3.6	11.5		
West	1	6/2/06	-90	-12.4	9.0	33.5	15.8
Kelowna	2	7/6/06	-66	-7.8	-4.2	54.8	20.2
	3	9/2/06	-89	-9.2	-15.2	4.0	**20.9**
49.89°N,	4	10/4/06	-85	-10.7	0.6	17.1	**15.6**
119.56°W	5	10/31/06	-89	-10.5	-4.7	15.7	**9.2**
580 masl	6	12/2/06	-137	-17.3	1.1	**36.1**	**4.8**
	7	1/4/07	-177	-23.0	7.3	**34.5**	**0.6**
	8	1/24/07	-117	-14.0	-5.7	10.0	-2.5
	9	4/30/07	-113	-13.8	-2.7	**18.5**	**5.9**
	10	6/20/07	-90	-11.1	-1.1	**54.3**	**16.3**
	11	6/26/07	-115	-14.7	2.6	19.5	16.5
	12	8/8/07	-76	-9.1	-3.6	69.7	22.3
	13	9/6/07	-81	-9.6	-4.0	9.4	19.1
	14	10/5/07	-110	-14.1	3.3	44.7	13.9
	15	10/21/07	-105	-14.2	9.0	22.6	9.6
	16	11/17/07	-95	-12.1	1.5	13.6	6.9
	17	12/29/07	-136	-17.7	5.4	**37.6**	**-0.5**
	18	2/22/08	-156	-20.3	6.2	**32.0**	**-1.0**
	19	3/28/08	-129	-16.7	4.5	8.6	**5.1**
		Minimum	-177	-23.0	-15.2		
		Maximum	-66	-7.8	9.0		
		Average	-108	-13.6	0.5		
		Std. dev.	29	4.0	6.1		

Amount-weighted annual δ^2H and $\delta^{18}O$ values for precipitation collected in the Okanagan Basin, BC, Canada, were calculated using the parameters provided in Table A.2.

Table A.2. Amount-weighted annual δ^2H and $\delta^{18}O$ values of Okanagan Basin precipitation.

Station	Sample	Date sampled (m/dd/yy)	Sampling interval	δ^2H (‰)	Weighted δ^2H (‰)	$\delta^{18}O$ (‰)	Weighted $\delta^{18}O$ (‰)	Total pptn (mm)
Osoyoos	1	4/19/06	3/2/06-4/19/06	-115	-5800	-14.4	-724.3	50.3
West	2	6/2/06	4/20/06-6/2/06	-89	-5069	-10.6	-606.4	57.1
	3	7/7/06	6/3/06-7/7/06	-81	-7202	-9.5	-839.8	88.4
49.05°N,	4	8/2/06	7/8/06-8/2/06	-102	-368	-11.3	-40.7	3.6
119.52°W	5	9/8/06	8/3/06-9/8/06	-91	-37	-11.2	-4.5	0.4
360 masl	7	11/2/06	10/5/06-11/2/06	-116	-2184	-13.1	-245.9	18.8
	8	12/16/06	11/3/06-12/16/06	-114	-9970	-15.6	-1363.8	87.2
	9	1/22/07	12/17/06-1/22/07	-150	-3561	-19.0	-453.3	23.8
	10	2/19/07	1/22/07-2/19/07	-144	-1616	-18.3	-204.4	11.2
	12	5/5/07	3/25/07-5/2/07	-113	-68	-13.4	-8.0	0.6
	14	10/5/07	8/18/07-10/5/07	-75	-2135	-6.1	-173.9	28.5
	16	12/29/07	11/18/07-12/29/07	-142	-6152	-18.9	-816.5	43.2
	17	1/27/08	12/30/07-1/27/08	-147	-4580	-18.7	-582.2	31.2
	18	3/8/08	1/28/08-3/8/08	-109	-1069	-12.7	-124.8	9.8
	19	4/24/08	3/9/08-4/24/08	-92	-865	-8.2	-77.1	9.4
					-50674		**-6265.5**	**463.5**
					-109		**-13.5**	
Osoyoos	1	3/1/06	2/1/06-3/1/06	-157	-5027	-18.3	-585.6	32.0
East	2	4/6/06	3/2/06-4/6/06	-111	-3541	-13.7	-437.0	31.9
	3	6/2/06	5/1/06-6/2/06	-86	-4429	-7.5	-386.8	51.5
49.03°N,	4	6/29/06	6/3/06-6/29/06	-95	-6850	-9.6	-690.7	72.1
119.40°W	5	11/7/06	10/3/06-11/7/06	-85	-1859	-9.6	-210.8	22.0
810 masl	6	12/8/06	11/8/06-12/8/06	-82	-3668	-11.5	-512.9	44.6
	7	6/11/07	6/1/07-6/11/07	-115	-3587	-13.4	-419.0	31.2
					-28961		**-3242.8**	**285.3**
					-102		**-11.4**	
West	1	6/2/06	5/20/06-6/2/06	-90	-3020	-12.4	-415.1	33.5
Kelowna	2	7/6/06	6/3/06-7/6/06	-66	-3632	-7.8	-425.2	54.8
	3	9/2/06	8/3/06-9/2/06	-89	-355	-9.2	-36.8	4.0
49.89°N,	4	10/4/06	9/3/06-10/4/06	-85	-1459	-10.7	-183.7	17.1
119.56°W	5	10/31/06	10/5/06-10/31/06	-89	-1396	-10.5	-165.3	15.7
580 masl	6	12/2/06	11/1/06-12/1/06	-137	-4957	-17.3	-624.5	36.1
	7	1/4/07	12/3/06-1/4/07	-177	-6096	-23.0	-793.5	34.5
	8	1/24/07	1/5/07-1/24/07	-117	-1174	-14.0	-139.6	10.0
	9	4/30/07	1/25/07-4/30/07	-113	-2095	-13.8	-255.7	18.5
	10	6/20/07	5/1/07-6/20/07	-90	-4897	-11.1	-604.4	54.3
	11	6/26/07	6/21/07-6/26/07	-115	-2245	-14.7	-287.0	19.5
	12	8/8/07	6/27/07-8/8/07	-76	-5317	-9.1	-633.6	69.7
	13	9/6/07	8/9/07-9/6/07	-81	-760	-9.6	-90.2	9.4
	14	10/5/07	9/7/07-10/5/07	-110	-4895	-14.1	-630.3	44.7
	15	10/21/07	10/06/07-10/21/07	-105	-2364	-14.2	-320.9	22.6
	16	11/17/07	10/22/07-11/17/07	-95	-1296	-12.1	-164.6	13.6
	17	12/29/07	11/18/07-12/29/07	-136	-5121	-17.7	-665.5	37.6
	18	2/22/08	12/30/07-2/22/08	-156	-5005	-20.3	-650.6	32.0
	19	3/28/08	2/23/08-3/28/08	-129	-1110	-16.7	-143.5	8.6
					-57194		**-7230.0**	**536.2**
					-107		**-13.5**	

Amount-weighted (approximate) monthly δ^2H and $\delta^{18}O$ values for precipitation collected in the Okanagan Basin, British Columbia, Canada, were calculated using the parameters provided in Table A.3.

Table A.3. Parameters used to calculate amount-weighted monthly δ^2H and $\delta^{18}O$ values.

Station	Sample	Approximate Month	Date sampled (m/dd/yy)	δ^2H (‰)	Weighted δ^2H (‰)	$\delta^{18}O$ (‰)	Weighted $\delta^{18}O$ (‰)	Total pptn (mm)
Osoyoos	10	January-February	2/19/07	-144	-1616	-18.3	-204.4	11.2
	1 (east)		3/1/06	-109	-1069	-12.7	-124.8	9.8
	18		3/8/08	-157	-5027	-18.3	-585.6	32.0
					-7712		**-914.8**	**53.0**
					-146		**-17.3**	
	1	March-April	4/19/06	-115	-5800	-14.4	-724.3	50.3
	2 (east)		4/6/06	-92	-865	-8.2	-77.1	9.4
	12		5/5/07	-111	-3541	-13.7	-437.0	31.9
	19		4/24/08	-113	-68	-13.4	-8.0	0.6
					-10273		**-1246.5**	**92.2**
					-111		**-13.5**	
	2	April-May	6/2/06	-86	-4429	-7.5	-386.8	51.5
	3 (east)		6/2/06	-89	-5069	-10.6	-606.4	57.1
					-9498		**-993.2**	**108.6**
					-87		**-9.1**	
	4 (east)	June	6/29/06	-95	-6850	-9.6	-690.7	72.1
	3		7/7/06	-81	-7202	-9.5	-839.8	88.4
	7 (east)		6/11/07	-115	-3587	-13.4	-419.0	31.2
					-17638		**-1949.5**	**191.7**
					-92		**-10.2**	
	4	July	8/2/06	-102	-368	-11.3	-40.7	3.6
					-368		**-40.7**	**3.6**
					-102		**-11.3**	
	5	August	9/8/06	-91	-37	-11.2	-4.5	0.4
					-37		**-4.5**	**0.4**
					-91		**-11.2**	
	14	September	10/5/07	-75	-2135	-6.1	-173.9	28.5
					-2135		**-173.9**	**28.5**
					-75		**-6.1**	
	7	October	11/2/06	-116	-2184	-13.1	-245.9	18.8
	5 (east)		11/7/06	-85	-1859	-9.6	-210.8	22.0
					-4043		**-456.7**	**40.8**
					-99		**-11.2**	
	8	November-	12/16/06	-114	-9970	-15.6	-1363.8	87.2
	6 (east)	December	12/8/06	-82	-3668	-11.5	-512.9	44.6
	16		12/29/07	-142	-6152	-18.9	-816.5	43.2
					-19790		**-2693.2**	**175.0**
					-113		**-15.4**	
	9	December-	1/22/07	-150	-3561	-19.0	-453.3	23.8
	17	January	1/27/08	-147	-4580	-18.7	-582.2	31.2
					-8141		**-1035.5**	**55.0**
					-148		**-18.8**	

Table A.3 continued

Station	Sample	Approximate Month	Date sampled (m/dd/yy)	δ^2H (‰)	Weighted δ^2H (‰)	$\delta^{18}O$ (‰)	Weighted $\delta^{18}O$ (‰)	Total pptn (mm)
West	8	January-February	1/24/07	-117	-1174	-14.0	-139.6	10.0
Kelowna	18		2/22/08	-156	-5005	-20.3	-650.6	32.0
					-6179		**-790.2**	**42.0**
					-147		**-18.8**	
	9	February-April	4/30/07	-113	-2095	-13.8	-255.7	18.5
	19		3/28/08	-129	-1110	-16.7	-143.5	8.6
					-3205		**-399.2**	**27.1**
					-118		**-14.7**	
	1	May-June	6/2/06	-90	-3020	-12.4	-415.1	33.5
	10		6/20/07	-90	-4897	-11.1	-604.4	54.3
	11		6/26/07	-115	-2245	-14.7	-287.0	19.5
	2		7/6/06	-66	-3632	-7.8	-425.2	54.8
					-13794		**-1731.7**	**162.1**
					-85		**-10.7**	
	12	July	8/8/07	-76	-5317	-9.1	-633.6	69.7
					-5317		**-633.6**	**69.7**
					-76		**-9.1**	
	3	August	9/2/06	-89	-355	-9.2	-36.8	4.0
	13		9/6/07	-81	-760	-9.6	-90.2	9.4
					-1115		**-127.0**	**13.4**
					-83		**-9.5**	
	4	September	10/4/06	-85	-1459	-10.7	-183.7	17.1
	14		10/5/07	-110	-4895	-14.1	-630.3	44.7
					-6353		**-813.9**	**61.8**
					-103		**-13.2**	
	5	October	10/31/06	-89	-1396	-10.5	-165.3	15.7
	15		10/21/07	-105	-2364	-14.2	-320.9	22.6
					-3760		**-486.2**	**38.3**
					-98		**-12.7**	
	6	November	12/2/06	-137	-4957	-17.3	-624.5	36.1
	16		11/17/07	-95	-1296	-12.1	-164.6	13.6
					-6253		**-789.1**	**49.7**
					-126		**-15.9**	
	7	December	1/4/07	-177	-6096	-23.0	-793.5	34.5
	17		12/29/07	-136	-5121	-17.7	-665.5	37.6
					-11217		**-1459.0**	**72.1**
					-156		**-20.2**	

APPENDIX B
SURFACE WATER DATA

δ^2H and $\delta^{18}O$ values of surface waters collected in the Okanagan Basin, British Columbia, Canada, are provided in Table B.1.

Table B.1. Field parameters (pH, temperature [Temp], total alkalinity [Alk]), δ^2H and $\delta^{18}O$ values of surface water samples collected in the Okanagan Basin between February 2006 and April 2008. Blank cell indicates parameter not analyzed. Red values discarded as samples may have been affected by evaporation during storage.

Station (ID)	Sample No.	Date Sampled (mm/dd/yy)	pH	Temp (ºC)	Alk (mg/l $CaCO_3$)	δ^2H (‰)	$\delta^{18}O$ (‰)
Ellison (2)	1	5/01/06	8.58	13.1	108	-104	-11.1
	2	6/01/06	8.43	16.9	110	-105	-12.0
	3	7/08/06	8.60		110	-105	-11.6
	4	8/01/06	8.56	22.6	102	-105	-10.6
	5	9/09/06	8.61	21.3	100	-103	-11.4
	6	10/07/06	8.31	15.7	102	-102	-10.7
	7	11/11/06			104	-101	-9.9
	8	12/10/06			102	-102	-11.5
	9	1/20/07			102	-101	-11.3
	10	3/25/07	8.33	6.8	104	-101	-11.6
	11	5/13/07	8.49	14.2	105	-102	-11.6
	12	6/17/07	8.48	15.3	104	-102	-11.8
	13	7/11/07	8.36	12.2	108		
	14	8/27/07	8.42	13.2	107	-101	-11.7
	15	11/15/07	8.22	7.8	90	-99	-11.2
	16	2/10/08				-108	-11.7
	17	3/08/08			109	-108	-10.7
	18	4/23/08	8.18	6.5	103	-108	-11.4
Mean (‰)						-103	-11.3
Std. Dev. (‰)						3	0.5
Min. (‰)						-108	-12.0
Max. (‰)						-99	-9.9
Range (‰)						9	2.1
Peachland (3)	1	6/05/06	8.45	16.9	92	-109	-11.9
	2	7/07/06	8.24	21.8	96	-105	-11.8
	3	8/04/06	8.29	20.8	95	-106	-10.7
	4	9/08/06	8.35	19.8	95	-104	-11.2
	5	10/08/06	8.60	15.7	101	-102	-10.7
	6	11/02/06	8.35	8.9	107	-98	-10.7
	7	12/05/06			104	-101	-11.8
	8	1/22/07	8.37	3.8	104	-101	-11.5
	9	2/16/07	9.16	5.9	109	-103	-11.8
	10	3/24/07	8.46	6.3	105	-101	-11.5
	11	5/06/07	8.83	11.3	105	-102	-11.9
	12	6/16/07	8.31	16.7	103	-104	-12.1
	13	7/15/07	8.36	25.4	101	-102	-11.9
	14	8/18/07	8.35	19.3	98	-102	-11.8
	15	10/05/07	8.35	15.2	99		
	16	11/17/07	7.55	9.1	76	-103	-11.7
	17	12/29/07	8.11	4.4	110	-100	-11.3

Table B.1 continued

Station (ID)	Sample No.	Date Sampled (mm/dd/yy)	pH	Temp (°C)	Alk (mg/l $CaCO_3$)	δ^2H (‰)	$\delta^{18}O$ (‰)
Peachland (3)	18	1/27/08	8.18	3.0		-107	-11.9
continued	19	3/08/08	8.07	7.9	108	-109	-11.7
	20	4/24/08	8.46	5.6		-109	-11.6
Mean (‰)						-103	-11.6
Std. Dev. (‰)						3	0.4
Min. (‰)						-109	-12.1
Max. (‰)						-98	-10.7
Range (‰)						11	1.4
Penticton (6)	1	5/01/06	8.50	10.8	110	-102	-11.3
	2	6/05/06	8.39	15.9	91	**-112**	**-9.9**
	3	7/07/06	8.41	27.3	100	-105	-11.9
	4	8/04/06	8.41	22.7	89	-103	-10.9
	5	9/08/06	8.43	20.4	102	-103	-10.9
	6	10/05/06	8.37	18.2	104	-103	-10.4
	7	11/02/06	8.23	7.7	105	-100	-10.9
	8	12/05/06			105	-100	-11.7
	9	1/22/07	8.28	3.1	102	-100	-11.4
	10	2/16/07	8.12	4.3	108	-102	-11.8
	11	3/24/07	8.26	5.1	109	-101	-11.4
	12	5/06/07	8.59	11.3	105	-103	-12.0
	13	6/16/07	8.33	17.2	101	-103	-11.8
	14	7/15/07	8.27	26.8	103	-103	-12.0
	15	8/18/07	8.36	21.7	98	-102	-11.8
	16	10/05/07	8.15	11.8	99		
	17	11/17/07	8.19	7.1	90	-102	-11.8
	18	12/29/07	8.27	4.3	112	-101	-11.4
	19	1/27/08	7.85	3.1		-108	-11.7
	20	3/08/08	8.30	5.9	108	-108	-11.4
	21	4/24/08	8.06	5.9		-108	-11.9
Mean (‰)						-103	-11.5
Std. Dev. (‰)						3	0.5
Min. (‰)						-108	-12.0
Max. (‰)						-100	-10.4
Range (‰)						8	1.6
OK Falls (7)	1	5/02/06	8.52	11.2	103	-102	-11.3
	2	6/05/06	8.39	16.0	95	-107	-12.5
	3	7/07/06	8.45	25.6	104	-105	-11.6
	4	8/04/06	8.45	22.3	98	-104	-10.7
	5	9/08/06	8.41	20.7	99	-103	-11.1
	6	10/04/06	8.35	15.9	102	-101	-10.1
	7	11/02/06	8.31	8.6	105	-100	-11.3
	8	12/09/06			104	-102	-11.6
	9	12/28/06				-99	-11.2
	10	1/22/07	8.37	1.6	104	-103	-11.6
	11	2/16/07	8.52	2.6	105	-101	-11.6
	12	3/24/07	8.52	5.7	105	-102	-11.8
	13	5/06/07	8.27	10.7	105	-102	-11.8
	14	6/16/07	8.53	19.1	104	-101	-11.7
	15	7/15/07	8.36	26.3	101	-102	-11.7
	16	8/18/07	8.51	21.6	97	-101	-11.5
	17	10/05/07	8.18	13.5	98		
	18	11/17/07	7.60	8.0	92	-102	-11.8

Table B.1 continued

Station (ID)	Sample No.	Date Sampled (mm/dd/yy)	pH	Temp (°C)	Alk (mg/l $CaCO_3$)	δ^2H (‰)	$\delta^{18}O$ (‰)
OK Falls (7)	19	12/29/07	8.10	3.3	112	-101	-11.7
continued	20	1/27/08	8.08	1.7		-106	-11.6
	21	3/08/08	8.26	5.5	109	-108	-11.0
	22	4/24/08	8.09	7.1		-107	-11.7
Mean (‰)						-103	-11.5
Std. Dev. (‰)						3	0.5
Min. (‰)						-107	-12.5
Max. (‰)						-99	-10.1
Range (‰)						8	2.4
Oliver (13)	1	2/28/06	8.24	12.3	90	-106	-11.5
	2	5/02/06	8.34	18.7	90	-111	-12.9
	3	6/05/06	8.40	25.0	102	-107	-13.5
	4	8/02/06	8.47	23.8	101	-104	-10.6
	5	9/08/06	8.23	21.6	100	-104	-10.8
	6	10/04/06	8.25	16.6	103	-102	-10.5
	7	11/02/06	8.35	6.5	116	-101	-11.5
	8	12/09/06			122	-102	-11.5
	9	1/22/07	8.18	1.8	120	-102	-11.6
	10	2/16/07	8.20	5.1	117	-101	-11.6
	11	3/24/07	8.40	8.1	112	-102	-11.7
	12	5/06/07	8.16	12.4	97	-106	-12.5
	13	6/16/07	8.30	20.0	104	-104	-12.3
	14	7/15/07	8.19	25.7	105	-103	-12.0
	15	8/18/07	8.56	21.5	99	-100	-11.6
	16	10/05/07	8.21	12.3	96		
	17	11/17/07	7.78	7.4	92	-103	-11.6
	18	12/29/07	7.84	2.3	126	-102	-11.9
	19	1/27/08	7.75	0.5		-108	-11.9
	20	3/08/08	8.12	9.3	113	-107	-10.6
	21	4/24/08	8.17	9.2		-109	-12.1
Mean (‰)						-104	-11.7
Std. Dev. (‰)						3	0.8
Min. (‰)						-111	-13.5
Max. (‰)						-100	-10.5
Range (‰)						11	3.0
Oroville (109)	1	6/05/06				-106	-12.2
	2	7/10/06				-106	-11.9
	3	8/06/06				-105	-11.4
	4	8/25/06				-106	-11.4
	5	11/07/06				-99	-11.5
	6	12/11/06				-100	-11.3
	7	12/28/06				-101	-11.3
	8	2/01/07				-101	-11.4
	9	3/08/07				-100	-11.7
	10	3/31/07				-101	-11.4
	11	5/01/07				-101	-11.5
	12	6/15/07				-102	-11.6
	13	6/29/07				-101	-11.6
	14	8/03/07				-99	-11.2
	15	2/23/08				-106	-11.1
	16	4/11/08				-106	-12.0

Table B.1 continued

Station (ID)	Sample No.	Date Sampled (mm/dd/yy)	pH	Temp (°C)	Alk (mg/l $CaCO_3$)	δ^2H (‰)	$\delta^{18}O$ (‰)
Mean (‰)						-102	-11.5
Std. Dev. (‰)						3	0.3
Min. (‰)						-106	-12.2
Max. (‰)						-99	-11.1
Range (‰)						8	1.0
Osoyoos Lake							
Mouth (15)	1	5/03/06	8.07	11.7	88	-110	-13.0
	2	5/31/06	8.18	17.1	74	-107	-13.5
	3	7/12/06	8.47	23.5	101	-102	-11.0
	4	8/02/06	8.04	21.0	104	-104	-11.5
	5	9/05/06				-105	-9.9
	6	10/05/06	8.08	13.3	114	-102	-11.5
Pumphouse (33)	1	3/06/06				-105	-11.4
	2	3/06/06				-106	-11.6
	3	5/03/06	8.32	10.8	110	-104	-11.5
	4	5/03/06	8.38	11.2	111	-102	-11.7
	5	5/31/06	8.35	17.6	87	-109	-12.9
	6	7/12/06	8.58	23.6	95	-107	-11.3
	7	8/02/06	8.37	21.7	97	-104	-11.6
	8	9/05/06				-105	-10.1
	9	10/05/06	8.28	14.1	103	-102	-10.9
Central Basin	1	5/03/06	8.40	12.1	115	-97	-11.6
(83)	2	5/31/06	8.37	18.8	89	-109	-12.9
	3	7/12/06	8.57	23.6	96	-106	-11.4
	4	8/02/06	8.43	23.0	97	-103	-11.6
	5	9/05/06				-103	-9.9
	6	10/05/06	8.26	16.3	105	-102	-10.8
Canada/US	1	5/03/06	8.33	13.3	111	-102	-11.2
Border	2	5/31/06	8.43	19.5	89	**-110**	**-8.9**
(107)	3	7/12/06	8.69	23.3	92	-105	-11.7
	4	8/02/06	8.51	23.4	98	-105	-10.9
	5	9/05/06				-103	-10.2
	6	10/05/06	8.12	16.7	108	-102	-10.6
Mean (‰)						-104	-11.4
Std. Dev. (‰)						3	0.9
Min. (‰)						-110	-13.5
Max. (‰)						-97	-9.9
Range (‰)						13	3.6
McKinney (14)	1	9/12/08				-130	-17.3
Spotted Lake (21)	1	5/27/06				-62	-2.2
Kettle Lake (49)	1	5/18/06	8.75	8.67	174	-90	-10.2
	2	7/27/06	8.66	8.73	156	-101	-10.7
	3	9/30/06	8.62	8.60	170	-101	-10.6
Wildhorse (51)	1	10/21/07				-66	-3.4
Blue Lake (55)	1	10/21/07				-53	-1.8
Peanut Pond (63)	1	5/18/06	8.64	8.70	162	-87	-4.7
	2	7/28/06	7.06	7.40	286	-85	-7.4
	3	9/30/06	7.11	7.31	284	-85	-7.3
Kilpoola Lk (67)	1	10/21/07				-49	-2.0
Taylor (69)	1	4/24/06				-120	-15.4
Chapman (75)	1	4/23/06				-124	-15.9
Haynes Ck. (99)	1	5/23/06				-125	-16.3
Yos Pond (105)	1	9/12/08				-116	-12.2

APPENDIX C
GROUNDWATER DATA

Geochemical data for groundwaters collected in the Okanagan Basin, British Columbia, Canada, are provided in Table C.1.

Table C.1. Geochemistry, age dates and aquifer data for groundwaters and irrigation user's water. All results in mg/l, except as noted. Number in brackets after well ID is sample number. Sample date: m/d/yy. Screened material abbrevs: Br = bedrock; SG = sand & gravel; SS = silty sand; CG = cobbles & gravel; Ob = overburden. Other abbrevs: Unk = not known; n/v = not available; n/a = not applicable. Blank cell: parameter not analyzed. Red values discarded: samples may have been affected by evaporation during storage.

Location	Valley Bottom and Benchlands											
Water System	North Portion of Study Area											
Well ID	25 (1)	25 (2)	25 (3)	26	27a (1)	27c (1)	27c (2)	27c (3)	27c (4)	28 (1)	28 (2)	28 (3)
Elevation (masl)	263	263	263	303	305	305	305	305	305	321	321	321
Well depth (masl)	256	256	256	289	300	293	293	293	293	303	303	303
Screened material	SG	SG	SG	Silt	SG	SS	SS	SS	SS	Silt	Silt	Silt
Aquifer No.	193	193	193	193	193	193	193	193	193	193	193	193
Date sampled	5/25/06	7/28/06	9/26/06	10/05/06	8/17/06	2/14/06	5/25/06	7/26/06	9/28/06	9/24/04	2/14/06	5/25/06
Field pH	7.60	7.62	7.47	7.14	7.25	7.50	7.43	7.31	7.29	7.24	7.32	7.17
Field HCO_3	342	379	404	337	256	430	410	417	451	401	381	419
pH	8.25		8.13	8.22	8.05		8.20	8.10	8.16			8.14
Alkalinity ($CaCO_3$)	296		354	300	227		355	365	354			360
HCO_3	361		432	366	277		433	445	432			439
CO_3	<1		<1	<1	<1		<1	<1	<1			<1
OH	<1		<1	<1	<1		<1	<1	<1			<1
Cl	28		49	10	7		5	7	5			31
NO_3 (N)	5.7		0.5	1.7	1.1		5.1	5	4.3			9.9
SO_4	95		80	36	31		270	280	290			56
Ca	85		98	92	75		92	94	95			110
Fe	0.005		<0.001	0.017	0.004		0.018	0.031	0.008			0.008
Mg	37		42	19	12		42	42	45			33
Mn	0.003		0.001	0.002	<0.001		0.022	0.073	0.017			0.003
K	4.7		5.3	4.2	5.3		5.6	6.1	5.3			5.6
Na	34		36	14	13		126	119	117			29
δ^2H (‰VSMOW)	-103	-114	-110	-104	-106	-108	-108	-113	-106	-106	-102	-103
$\delta^{18}O$ (‰VSMOW)	-12.5	-10.8	-11.7	-10.4	-11.3	-12.2	-12.1	-11.5	-11.0	-10.5	-11.7	-11.7
^3H (TU)										11.6		
$^3H/^3He$ (TU)										3.3		
$^3H/^3He$ age (yr)										4.5		
^{14}C (pmC)												
CRA (yr BP)												
$\delta^{13}C$ (‰VPDB)												

Table C.1 continued

Location	Valley Bottom and Benchlands											
Water System	North Portion of Study Area											
Well ID	28 (4)	28 (5)	29a (1)	29a (2)	29a (3)	29a (4)	29a (5)	29b (1)	29b (2)	30 (1)	30 (2)	30 (3)
Elevation (masl)	321	321	318	318	318	318	318	318	318	318	318	318
Well depth (masl)	303	303	311	311	311	311	311	301	301	301	301	301
Screened material	Silt	Silt	Silt	Silt	Silt	Silt	Silt	Silt	Silt	Silt	Silt	Silt
Aquifer No.	193	193	193	193	193	193	193	193	193	193	193	193
Date sampled	7/26/06	9/28/06	2/14/06	5/24/06	7/26/06	9/27/06	2/16/07	7/29/06	9/30/06	9/24/04	2/14/06	5/25/06
Field pH	7.08	7.04	7.22	7.41	7.36	7.29	7.35	7.80	7.73	7.31	7.28	7.17
Field HCO_3	391	398		427	430	427	498	338	340	405	397	403
pH	7.94	7.98		8.12	8.08	8.10	7.89	8.20	8.28			8.14
Alkalinity ($CaCO_3$)	346	340		373	367	333	422	308	302			350
HCO_3	422	415		455	448	406	515	376	368			427
CO_3	<1	<1		<1	<1	<1	<1	<1	<1			<1
OH	<1	<1		<1	<1	<1	<1	<1	<1			<1
Cl	22	20		19	13	13	14	10	11			20
NO_3 (N)	10.2	9.3		5	7	7.7	2.9	0.4	1.4			15
SO_4	49	47		180	68	61	83	99	110			68
Ca	105	89		81	74	65	70	50	48			126
Fe	0.012	0.012		0.091	0.002	0.013	0.02	0.013	0.004			0.002
Mg	29	32		35	34	36	32	48	50			29
Mn	0.027	<0.001		2.47	1.41	1.17	1.07	0.73	0.41			0.003
K	6.0	5.2		5.2	5.6	4.8	5.6	7.9	7.5			7.3
Na	26	27		123	62	56	98	37	41			20
δ^2H (‰VSMOW)	-1085	-102	-104	-107	-102	-103	-104	-117	-110	-107	-104	-103
$\delta^{18}O$ (‰VSMOW)	-10.8	-12.7	-11.8	-12.2	-11.8	-12.6	-11.8	-12.1	-11.7	-11.9	-10.2	-11.3
^3H (TU)										11.4		
$^3H/^3He$ (TU)										0.4		
$^3H/^3He$ age (yr)										0.6		
^{14}C (pmC)												
CRA (yr BP)												
$\delta^{13}C$ (‰VPDB)												

Table C.1 continued

Location	Valley Bottom and Benchlands											
Water System	North Portion of Study Area											
Well ID	30 (4)	30 (5)	30 (6)	30 (7)	30 (8)	31b (1)	31b (2)	31b (3)	31b (4)	31b (5)	32 (1)	32 (2)
Elevation (masl)	318	318	318	318	318	321	321	321	321	321	281	281
Well depth (masl)	301	301	301	301	301	312	312	312	312	312	277	277
Screened material	Silt	Silt	Silt	Silt	Silt	Silt	Silt	Silt	Silt	Silt	SG	SG
Aquifer No.	193	193	193	193	193	193	193	193	193	193	193	193
Date sampled	5/25/06	7/26/06	7/26/06	9/27/06	9/27/06	2/14/06	5/24/06	7/26/06	9/27/06	2/16/07	6/03/06	9/30/06
Field pH	7.17	7.13	7.13	7.11	7.11	7.45	7.23	7.16	7.17	7.37	7.51	7.34
Field HCO_3	403	441	441	403	403	388	391	388	401	402	189	213
pH	8.02	7.96	7.98	8.02	7.99		8.10	8.03	8.03	7.88	7.99	8.11
Alkalinity ($CaCO_3$)	349	390	399	346	305		332	336	342	331	158	190
HCO_3	426	476	487	422	372		405	410	417	404	193	232
CO_3	<1	<1	<1	<1	<1		<1	<1	<1	<1	<1	<1
OH	<1	<1	<1	<1	<1		<1	<1	<1	<1	<1	<1
Cl	19	16	14	15	14		14	14	14	12	42	55
NO_3 (N)	15	8.1	7.5	14.7	12.9		6.9	9	9.7	10	3.2	4.3
SO_4	70	56	55	56	57		72	60	56	49	61	76
Ca	127	123	123	95	107		91	93	96	99	54	68
Fe	0.018	0.003	0.005	0.004	0.004		0.01	<0.001	<0.001	0.001	0.028	0.003
Mg	29	29	29	27	28		29	31	32	30	15	18
Mn	<0.001	0.003	0.016	<0.001	<0.001		0.05	0	0	0.001	0.016	0.001
K	7.3	7.7	8.3	7.0	7.1		5.6	6.5	5.7	6.1	2.6	2.7
Na	20	21	21	20	21		40	30	33	23	38	48
δ^2H (‰VSMOW)	-100	-107		-100.3		-104	-104	-95	-101	-101	-102	-103
$\delta^{18}O$ (‰VSMOW)	-12.1	-11.7		-11.6		-11.6	-11.8	-11.9	-11.5	-11.2	-11.7	-12.0
^3H (TU)												
$^3H/^3He$ (TU)												
$^3H/^3He$ age (yr)												
^{14}C (pmC)												
CRA (yr BP)												
$\delta^{13}C$ (‰VPDB)												

Table C.1 continued

Location	Valley Bottom and Benchlands												
Water System	North Portion of Study Area												
Well ID	35 (1)	35 (2)	35 (3)	35 (4)	37 (1)	37 (2)	37 (3)	39 (1)	39 (2)	39 (3)	39 (4)	39 (5)	39 (6)
Elevation (masl)	296	296	296	296	290	290	290	318	318	318	318	318	318
Well depth (masl)	289	289	289	289				306	306	306	306	306	306
Screened material	Silt	Silt	Silt	Silt	SG	SG	SG	Silt	Silt	Silt	Silt	Silt	Silt
Aquifer No.	193	193	193	193	193	193	193	193	193	193	193	193	193
Date sampled	2/16/06	5/27/06	7/27/06	9/28/06	5/17/06	7/25/06	9/28/06	9/24/04	2/16/06	5/25/06	7/27/06	9/28/06	2/16/07
Field pH	7.52	7.35	7.02	6.96	7.27	7.24	7.37	7.46	7.51	7.37	7.16	7.15	7.42
Field HCO_3	331	333	379	473	272	271	300	298	320	318	314	299	304
pH		8.11	8.00	7.99	8.09		8.14			8.15	8.02	8.08	7.93
Alkalinity ($CaCO_3$)		295	334	390	237		232			269	270	250	249
HCO_3		360	407	476	289		283			328	329	305	304
CO_3		<1	<1	<1	<1		<1			<1	<1	<1	<1
OH		<1	<1	<1	<1		<1			<1	<1	<1	<1
Cl		25	22	25	25		28			12	14	9	11
NO_3 (N)		6.8	3.8	0.3	14		10.4			5	6.3	0.3	4.1
SO_4		65	67	87	150		120			62	54	47	52
Ca		103	109	123	128		112			84	90	80	77
Fe		0.003	0.015	0.015	0.009		<0.001			0.011	0.003	0.003	0.011
Mg		22	24	28	24		22			22	18	16	20
Mn		2.62	5.8	7.89	0.015		<0.001			0.012	0.009	0.005	<0.001
K		7.5	7.8	6.7	5.1		4.9			4.9	6.6	5.7	5.2
Na		22	22	31	24		23			25	23	22	24
δ^2H (‰VSMOW)	-108	-104	-106	-101	-101	-106	-102	-105	**-93**	-104	-103	-104	
$\delta^{18}O$ (‰VSMOW)	-11.7	-12.1	-11.8	-11.1	-10.9	-13.0	-12.9	-10.3	**-12.1**	-11.4	-11.2	-11.7	
^3H (TU)								13.7					
$^3H/^3He$ (TU)								15.6					
$^3H/^3He$ age (yr)								13.6					
^{14}C (pmC)													
CRA (yr BP)													
$\delta^{13}C$ (‰VPDB)													

Table C.1 continued

Location	Valley Bottom and Benchlands											
Water System	Central Portion of Study Area											
Well ID	42 (1)	42 (2)	42 (3)	43 (1)	43 (2)	43 (3)	44 (1)	44 (2)	44 (3)	46 (1)	46 (2)	52 (1)
Elevation (masl)	287	287	287	274	274	274	279	279	279	300	300	285
Well depth (masl)	281	281	281	271	271	271	273	273	273			281
Screened material	SG	SG	SG	SG	SG	SG	SG	SG	SG	SG	SG	SG
Aquifer No.	193	193	193	193	193	193	193	193	193	193	193	193
Date sampled	6/13/06	7/27/06	9/26/06	6/13/06	7/27/06	9/26/06	6/13/06	7/27/06	9/26/06	6/13/06	7/27/06	6/02/06
Field pH	7.17	7.12	7.05	7.46	7.21	7.28	7.6	7.33	7.15	7.3	7.11	7.29
Field HCO_3	366	331	373	369	235	351		283	267	412	440	354
pH	7.99		8.02	8.08		8.11	8.10		8.07	8.04		7.92
Alkalinity ($CaCO_3$)	331		299	206		223	250		250	349		307
HCO_3	404		365	251		272	305		305	426		375
CO_3	<1		<1	<1		<1	<1		<1	<1		<1
OH	<1		<1	<1		<1	<1		<1	<1		<1
Cl	7		6	10		6	6		6	6		23
NO_3 (N)	5.2		6.8	2.5		3.4	7.3		2.7	6.1		6.1
SO_4	50		41	55		36	42		40	33		90
Ca	114		105	72		68	75		75	105		116
Fe	0.002		0.001	<0.001		<0.001	0.001		<0.001	<0.001		0.001
Mg	20		17	17		16	24		19	28		24
Mn	0.002		<0.001	<0.001		<0.001	0.002		0.008	0.006		<0.001
K	4.8		4.8	4.2		4.0	3.5		4.1	4.6		4.3
Na	16		17	14		16	16		18	17		21
δ^2H (‰VSMOW)		-108	-99		-107	-101		-104	-101		-105	-102
$\delta^{18}O$ (‰VSMOW)		-11.4	-10.8		-10.5	-11.0		-11.2	-12.2		-11.5	-11.5
^3H (TU)												
$^3H/^3He$ (TU)												
$^3H/^3He$ age (yr)												
^{14}C (pmC)												
CRA (yr BP)												
$\delta^{13}C$ (‰VPDB)												

Table C.1 continued

Location	Valley Bottom and Benchlands											
Water System	Central Portion of Study Area											
Well ID	52 (3)	52 (4)	54a (1)	54a (2)	54a (3)	54a (4)	54a (5)	54b (1)	54b (2)	54b (3)	54b (4)	57 (1)
Elevation (masl)	285	285	288	288	288	288	288	288	288	288	288	323
Well depth (masl)	281	281	278	278	278	278	278	277	277	277	277	318
Screened material	SG	SG	SG	SG	SG	SG	SG	SG	SG	SG	SG	SG
Aquifer No.	193	193	193	193	193	193	193	193	193	193	193	193
Date sampled	7/27/06	10/04/06	9/24/04	2/16/06	5/25/06	7/27/06	9/26/06	2/28/06	5/25/06	7/27/06	9/26/06	7/26/06
Field pH	7.1	7.05	7.23	7.36	7.27	7.07	6.96	7.31	7.26	7.05	6.96	7.21
Field HCO_3	391	421	413	371	351	371	390	381	341	375	388	365
pH		8.14			8.15		7.94		8.12		7.95	
Alkalinity ($CaCO_3$)		372			299		336		301		335	
HCO_3		454			365		410		367		409	
CO_3		<1			<1		<1		<1		<1	
OH		<1			<1		<1		<1		<1	
Cl		20			16		16		15		17	
NO_3 (N)		7.3			6.2		7.5		5.3		7.2	
SO_4		76			92		110		93		120	
Ca		127			96		107		94		108	
Fe		0.002			0.002		0.003		<0.001		<0.001	
Mg		27			33		37		32		38	
Mn		<0.001			<0.001		0.003		0.008		<0.001	
K		5.2			5.1		5.7		5.0		5.7	
Na		29			23		29		23		29	
δ^2H (‰VSMOW)	-103	-102	-105	-103	-101	-104	-102	-104	-100	-1037	-1024	-102
$\delta^{18}O$ (‰VSMOW)	-12.3	-11.7	-11.7	-11.5	-11.8	-12.1	-11.5	-11.6	-11.1	-11.1	-12.1	-11.7
^3H (TU)												
$^3H/^3He$ (TU)												
$^3H/^3He$ age (yr)												
^{14}C (pmC)												
CRA (yr BP)												
$\delta^{13}C$ (‰VPDB)												

Table C.1 continued

Location	Valley Bottom and Benchlands													
Water System	Central Portion			South Portion of Study Area										
Well ID	57 (2)	57 (3)	57 (4)	61 (1)	61 (2)	61 (3)	61 (4)	61 (5)	62a (1)	62a (2)	62a (3)	62a (4)	62a (5)
Elevation (masl)	323	323	323	292	292	292	292	292	290	290	290	290	290
Well depth (masl)	318	318	318	278	278	278	278	278	279	279	279	279	279
Screened material	SG	SG	SG	SG	SG	SG	SG	SG	SG	SG	SG	SG	SG
Aquifer No.	193	193	193	193	193	193	193	193	193	193	193	193	193
Date sampled	2/28/06	5/17/06	9/28/06	9/24/04	2/15/06	5/26/06	7/28/06	9/29/06	9/24/04	2/15/06	5/26/06	7/28/06	9/29/06
Field pH	7.29	7.39	7.32	7.31	7.79	7.34	7.24	7.18	7.41	7.50	7.30	7.23	7.18
Field HCO_3	407	443	280	315	340	338	326	299	281	320	344	283	287
pH		8.18	8.16			8.14		8.06			8.15		8.06
Alkalinity ($CaCO_3$)		406	238			291		244			267		237
HCO_3		495	290			355		298			326		289
CO_3		<1	<1			<1		<1			<1		<1
OH		<1	<1			<1		<1			<1		<1
Cl		13	9			19		42			28		34
NO_3 (N)		3.8	2.2			5.5		4.3			3.7		2.5
SO_4		83	52			55		56			64		56
Ca		122	71			103		96			93		86
Fe		<0.001	<0.001			<0.001		<0.001			0.002		0.001
Mg		36	22			17		16			19		16
Mn		0.002	<0.001			<0.001		<0.001			0.006		0.003
K		4.0	3.1			4.8		4.2			5.0		4.5
Na		21	15			27		24			29		26
δ^2H (‰VSMOW)	-98	-97	-100	-105	-104	-103	-105	-105	-99	-103	-98	-96	-96
$\delta^{18}O$ (‰VSMOW)	-11.2	-12.1	-11.6	-10.8	-12.6	-8.2	-11.8	-10.7	-7.6	-10.7	-10.2	-9.0	-6.8
^3H (TU)				10.7					8.7				
$^3H/^3He$ (TU)				0.3					0.7				
$^3H/^3He$ age (yr)				0.5					1.4				
^{14}C (pmC)													
CRA (yr BP)													
$\delta^{13}C$ (‰VPDB)													

Table C.1 continued

Location	Valley Bottom and Benchlands											
Water System	South Portion of Study Area											
Well ID	62b (1)	62b (2)	62b (3)	62b (4)	62b (5)	66a (1)	66a (2)	66a (3)	66a (4)	66a (5)	66a (6)	66b (1)
Elevation (masl)	290	290	290	290	290	306	306	306	306	306	306	306
Well depth (masl)	281	281	281	281	281	295	295	295	295	295	295	297
Screened material	SG	SG	SG	SG	SG	SG	SG	SG	SG	SG	SG	SG
Aquifer No.	193	193	193	193	193	193	193	193	193	193	193	193
Date sampled	9/24/04	2/15/06	5/26/06	7/28/06	9/29/06	9/24/04	2/17/06	5/26/06	7/28/06	9/26/06	9/26/06	9/24/04
Field pH	7.44	7.42	7.50	7.45	7.27		7.22	7.25	7.18	7.10	7.10	7.29
Field HCO_3	298	287	304	285	307		332	308	348	362	362	325
pH			8.16		8.11			8.11		8.04	8.01	
Alkalinity ($CaCO_3$)			243		254			288		289	293	
HCO_3			296		310			351		353	357	
CO_3			<1		<1			<1		<1	<1	
OH			<1		<1			<1		<1	<1	
Cl			34		31			22		27	25	
NO_3 (N)			0.19		0.1			6.5		9.5	11.1	
SO_4			59		33			57		57	57	
Ca			67		60			109		112	114	
Fe			0.034		0.23			<0.001		<0.001	0.001	
Mg			25		22			16		18	18	
Mn			0.17		0.19			0.002		0.003	0.003	
K			6.3		5.8			4.7		5.1	5.0	
Na			28		34			23		24	23	
δ^2H (‰VSMOW)	-88	-90	-87	-89	-88		-101	-101	-103	-103		-106
$\delta^{18}O$ (‰VSMOW)	-9.3	-8.6	-11.7	-11.5	-11.4		-11.6	-11.8	-11.2	-11.4		-11.6
^3H (TU)	11.8					11.7						
$^3H/^3He$ (TU)	0.2					1.4						
$^3H/^3He$ age (yr)	0.4					2.0						
^{14}C (pmC)												
CRA (yr BP)												
$\delta^{13}C$ (‰VPDB)												

Table C.1 continued

Location	Valley Bottom and Benchlands										
Water System	South Portion of Study Area										
Well ID	66b (2)	66b (3)	66b (4)	66b (5)	70 (1)	70 (2)	70 (3)	70 (4)	70 (5)	72a (1)	72a (2)
Elevation (masl)	306	306	306	306	308	308	308	308	308	305	305
Well depth (masl)	297	297	297	297	300	300	300	300	300	294	294
Screened material	SG	SG	SG	SG	SG	SG	SG	SG	SG	SG	SG
Aquifer No.	193	193	193	193	193	193	193	193	193	193	193
Date sampled	2/16/06	5/26/06	7/28/06	9/26/06	9/24/04	2/16/06	5/26/06	7/28/06	9/26/06	5/26/06	7/28/06
Field pH	7.21	7.25	7.19	7.08	7.34	7.08	7.28	7.21	7.04	7.44	7.30
Field HCO_3	346	327	285	352	315	320	275	310	355	277	299
pH		8.10		8.02			8.18		7.95	8.22	
Alkalinity ($CaCO_3$)		278		299			246		284	228	
HCO_3		339		365			300		346	278	
CO_3		<1		<1			<1		<1	<1	
OH		<1		<1			<1		<1	<1	
Cl		22		25			26		31	10	
NO_3 (N)		5.8		9.3			10		24.4	2.6	
SO_4		56		58			55		78	42	
Ca		105		112			103		135	73	
Fe		<0.001		0.001			0.003		0.001	0.003	
Mg		16		18			16		22	18	
Mn		<0.001		<0.001			0.006		<0.001	0.002	
K		5.2		6.0			4.3		5.0	3.3	
Na		22		27			21		27	15	
δ^2H (‰VSMOW)	-101	-99	-102	-102	-101	-105	-101	-107	-104	-103	-99
$\delta^{18}O$ (‰VSMOW)	-10.9	-11.2	-11.4	-11.7	-11.7	-12.2	-10.9	-11.7	-11.8	-11.2	-10.6
^3H (TU)					9.9						
$^3H/^3He$ (TU)					3.2						
$^3H/^3He$ age (yr)					5.0						
^{14}C (pmC)											
CRA (yr BP)											
$\delta^{13}C$ (‰VPDB)											

Table C.1 continued

Location	Valley Bottom and Benchlands											
Water System	South Portion of Study Area											
Well ID	72a (3)	72a (4)	72a (5)	72b (1)	72b (2)	72b (3)	72b (4)	74a (1)	74a (2)	74a (3)	74a (4)	74a (5)
Elevation (masl)	305	305	305	305	305	305	305	305	305	305	305	305
Well depth (masl)	294	294	294	300	300	300	300	298	298	298	298	298
Screened material	SG	SG	SG	SG	SG	SG	SG	SG	SG	SG	SG	SG
Aquifer No.	193	193	193	193	193	193	193	193	193	193	193	193
Date sampled	9/24/04	2/16/06	9/27/06	9/24/04	5/26/06	7/28/06	9/27/06	9/24/04	2/16/06	5/26/06	7/28/06	9/29/06
Field pH	7.30	7.48	7.21	7.27	7.42	7.23	7.15	7.32	7.31	7.31	7.39	7.12
Field HCO_3	291	283	291	288	241	318	285	342	430	287	247	305
pH			8.05		8.21		8.08			8.11		8.01
Alkalinity ($CaCO_3$)			252		219		223			257		270
HCO_3			307		267		272			314		329
CO_3			<1		<1		<1			<1		<1
OH			<1		<1		<1			<1		<1
Cl			9		10		17			28		34
NO_3 (N)			1		1.9		0.9			16		15.8
SO_4			38		39		37			78		73
Ca			77		71		74			110		111
Fe			<0.001		0.009		0.006			<0.001		0.002
Mg			16		16		15			20		20
Mn			<0.001		<0.001		0.006			0.002		<0.001
K			3.6		3.2		3.6			6.3		6.7
Na			15		14		15			28		30
δ^2H (‰VSMOW)	-100	-103	-99	-100	-105	-101	-99	-105	-100	-103	-108	-103
$\delta^{18}O$ (‰VSMOW)	-11.4	-11.2	-11.2	-11.3	-11.6	-10.9	-11.2	-11.4	-11.5	-11.7	-11.4	-11.3
^3H (TU)												
$^3H/^3He$ (TU)												
$^3H/^3He$ age (yr)												
^{14}C (pmC)												
CRA (yr BP)												
$\delta^{13}C$ (‰VPDB)												

Table C.1 continued

Location	Valley Bottom and Benchlands											
Water System	South Portion of Study Area						Deep Confined Aquifer				Oliver	
Well ID	74b (1)	74b (2)	74b (3)	74b (4)	74b (5)	74b (6)	24 (1)	24 (2)	24 (3)	24 (4)	10 (1)	9 (1)
Elevation (masl)	305	305	305	305	305	305	286	286	286	286	304	303
Well depth (masl)	297	297	297	297	297	297	238	238	238	238		
Screened material	SG	SG	SG	SG	SG	SG	CG	CG	CG	CG	SG	SG
Aquifer No.	193	193	193	193	193	193	n/v	n/v	n/v	n/v	256	256
Date sampled	9/24/04	2/16/06	5/26/06	5/26/06	7/28/06	9/26/06	6/02/06	8/02/06	9/30/06	4/23/08	4/23/08	4/23/08
Field pH		7.32	7.32	7.32	7.30	7.06	7.95	7.90	7.64		7.20	7.28
Field HCO_3		313	327	327	276	300	313	305	297		272	258
pH			8.17	8.12		7.99	8.17	8.22	8.22			
Alkalinity ($CaCO_3$)			266	267		268	265	269	270			
HCO_3			325	326		327	323	328	329			
CO_3			<1	<1		<1	<1	<1	<1			
OH			<1	<1		<1	<1	<1	<1			
Cl			30	30		34	6	6	7			
NO_3 (N)			15	15		15.6	0	0	0.2			
SO_4			83	83		69	160	160	170			
Ca			115	117		109	75	85	78			
Fe			0.002	0.002		0.004	0.017	0.026	0.055			
Mg			21	21		20	39	40	41			
Mn			0.002	0.002		0.002	0.093	0.07	0.084			
K			6.9	6.9		7.1	5.5	5.8	5.2			
Na			28	28		31	28	29	29			
δ^2H (‰VSMOW)		-102	-101		-108	-102	-107	-108	-106	-112	-109	-107
$\delta^{18}O$ (‰VSMOW)		-11.5	-11.2		-9.6	-11.1	-12.8	-11.1	-11.2	-12.5	-12.0	-11.2
^3H (TU)	12.5									13.4±1.0	10.4±1.0	8.9±1.0
$^3H/^3He$ (TU)	0.9											
$^3H/^3He$ age (yr)	1.3											
^{14}C (pmC)										88.25±0.26		
CRA (yr BP)										948±20		
$\delta^{13}C$ (‰VPDB)										-12.3		

Table C.1 continued

Location	Valley Bottom and Benchlands											
Water System	--Summerland--		Vaseux	------Irrigation Tap User------			------Pumphouse #8------			------Pumphouse #9------		
Well ID	4 (1)	5 (1)	8 (1)									
Irrigation ID				36 (1)	36 (2)	36 (3)	47 (1)	47 (2)	47 (3)	88 (1)	88 (2)	88 (3)
Elevation (masl)	333	366	446	318	318	318	271	271	271	283	283	283
Well depth (masl)				n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Screened material	SG	SG	SG	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Aquifer No.	297	297	257	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Date sampled	9/28/04	9/28/04	9/27/04	5/31/06	7/26/06	9/28/06	5/31/06	7/28/06	9/29/06	5/31/06	7/28/06	9/29/06
Field pH				7.66	7.43	7.81	7.69	7.47	7.97	7.93	8.06	7.99
Field HCO_3				86	95	104	95	98		86	95	103
pH						8.21						
Alkalinity ($CaCO_3$)						112						
HCO_3						137						
CO_3						<1						
OH						<1						
Cl						7						
NO_3 (N)						0						
SO_4						29						
Ca						33						
Fe						<0.001						
Mg						9.2						
Mn						<0.001						
K						2.2						
Na						11						
δ^2H (‰VSMOW)	-129	-123	-121	-106	-108	-102	-105	-107	-101	**-107**	-105	-102
$\delta^{18}O$ (‰VSMOW)	-16.5	-16.1	-14.8	-12.8	-12.1	-10.9	-12.0	-12.2	-11.2	**-8.7**	-11.9	-10.6
^3H (TU)												
$^3H/^3He$ (TU)												
$^3H/^3He$ age (yr)												
^{14}C (pmC)												
CRA (yr BP)												
$\delta^{13}C$ (‰VPDB)												

Table C.1 continued

Location	Valley Bottom and Benchlands			Highlands								
Water System	Upper Benchland			Kilpoola Mountain								
Well ID	38 (1)	38 (2)	38 (3)	16 (1)	17 (1)	18 (1)	19 (1)	20 (1)	22 (1)	22 (2)	22 (3)	23 (1)
Elevation (masl)	427	427	427	654	638	652	652	643	687	687	687	677
Well depth (masl)	421	421	421	563	436		530	613	626	626	626	671
Screened material	Ob	Ob	Ob	Br	Br	Br	Br	Br	Br	Br	Br	Br
Aquifer No.	193?	193?	193?	248	248	248	248	248	248	248	248	248
Date sampled	5/17/06	7/27/06	9/29/06	8/18/07	8/18/07	8/18/07	8/18/07	8/18/07	8/18/07	10/21/07	4/24/08	10/21/07
Field pH	7.40	7.50	7.42								7.30	
Field HCO_3	391	409	402								242	
pH	8.14	8.13	8.07									
Alkalinity ($CaCO_3$)	338	356	320									
HCO_3	412	434	390									
CO_3	<1	<1	<1									
OH	<1	<1	<1									
Cl	58	31	22									
NO_3 (N)	0.11	0	0									
SO_4	58	46	42									
Ca	107	113	105									
Fe	0.003	0.02	<0.001									
Mg	20	18	16									
Mn	0.001	0.057	<0.001									
K	3.7	3.8	2.8									
Na	50	32	26									
δ^2H (‰VSMOW)	-121	-124	-121	-131	-149	-123	-139	-126	-125	-125	-130	-123
$\delta^{18}O$ (‰VSMOW)	-16.1	-15.5	-15.3	-17.1	-19.6	-16.2	-18.7	-16.7	-16.5	-16.5	-16.3	-16.5
^3H (TU)											4.2±0.5	
$^3H/^3He$ (TU)												
$^3H/^3He$ age (yr)												
^{14}C (pmC)											67.83±0.17	
CRA (yr BP)											3062±20	
$\delta^{13}C$ (‰VPDB)											-13.2	

Table C.1 continued

Location	Highlands										
Water System	Kilpoola Mountain				Bridesville				Anarchist Mountain		
Well ID	40 (1)	41 (1)	48 (1)	50 (1)	45 (1)	53 (1)	56 (1)	71 (1)	58 (1)	59 (1)	60 (1)
Elevation (masl)	451	518	680	871	1030	1038	1354	1043	941	969	1026
Well depth (masl)	448	515			1024	1034	1262	1017	837	878	
Screened material	Br	Br	Br	Br	Br	Br	Br	Br	Br	Br	Br
Aquifer No.	248	248	248	248	n/v	n/v	n/v	n/v	808	808	808
Date sampled	10/21/07	10/21/07	10/21/07	10/21/07	8/06/06	9/12/08	9/12/08	9/12/08	6/04/06		6/04/06
Field pH											
Field HCO_3											
pH											
Alkalinity ($CaCO_3$)											
HCO_3											
CO_3											
OH											
Cl											
NO_3 (N)											
SO_4											
Ca											
Fe											
Mg											
Mn											
K											
Na											
δ^2H (‰VSMOW)	-123	-124	-124	-67	-133	-137	-144	-138	-130	-124	-132
$\delta^{18}O$ (‰VSMOW)	-16.3	-16.1	-16.5	-3.5	-16.8	-17.3	-18.9	-17.6	-16.8	-16.0	-17.0
^3H (TU)											
$^3H/^3He$ (TU)											
$^3H/^3He$ age (yr)											
^{14}C (pmC)											
CRA (yr BP)											
$\delta^{13}C$ (‰VPDB)											

Table C.1 continued

Location	Highlands											
Water System	Anarchist Mountain											
Well ID	64 (1)	65 (1)	68 (1)	73 (1)	76 (1)	77 (1)	78 (1)	79 (1)	80 (1)	84 (1)	85 (1)	86 (1)
Elevation (masl)	941	1146	850	801	728	837	810	1186	920	1218	1123	1221
Well depth (masl)	932	1122	826	687	618		700	1070	829	1121		1062
Screened material	Br	Br	Br	Br	Br	Br	Br	Br	Br	Br	Br	Br
Aquifer No.	808	810	808	808	808	808	808	810	808	810	n/v	810
Date sampled	5/05/06	9/12/08	9/11//08	5/05/06	5/05/06	8/4/08	4/23/06	9/12/08	9/04/06	9/12/08	8/16/06	9/12/08
Field pH												
Field HCO_3												
pH												
Alkalinity ($CaCO_3$)												
HCO_3												
CO_3												
OH												
Cl												
NO_3 (N)												
SO_4												
Ca												
Fe												
Mg												
Mn												
K												
Na												
δ^2H (‰VSMOW)	-128	-137	-133	-127	-126	-134	-133	-145	-129	-138	-135	-144
$\delta^{18}O$ (‰VSMOW)	-16.5	-17.3	-16.7	-15.8	-16.1	-16.9	-16.5	-18.7	-16.6	-17.8	-15.5	-18.0
^3H (TU)												
$^3H/^3He$ (TU)												
$^3H/^3He$ age (yr)												
^{14}C (pmC)												
CRA (yr BP)												
$\delta^{13}C$ (‰VPDB)												

Table C.1 continued

Location	Highlands										
Water system	Anarchist Mountain										
Well ID	87 (1)	89 (1)	89 (2)	90 (1)	91 (1)	92 (1)	93 (1)	93 (2)	94 (1)	95 (1)	96 (1)
Elevation (masl)	1128	510	510	985	1129	1143	763	763	1148	764	772
Well depth (masl)		388	388						1086	663	635
Screened material	Br	Br	Br	Br	Br	Br	Br	Br	Br	Br	Br
Aquifer No.	810	808	808	808	n/v	n/v	808	808	n/v	808	808
Date sampled	9/12/08	4/24/08	4/26/06	4/24/08	8/16/06	8/16/06	7/26/06	11/20/07	9/12/08	5/17/06	4/23/06
Field pH		7.07		7.12							
Field HCO_3		138		199							
pH											
Alkalinity ($CaCO_3$)											
HCO_3											
CO_3											
OH											
Cl											
NO_3 (N)											
SO_4											
Ca											
Fe											
Mg											
Mn											
K											
Na											
δ^2H (‰VSMOW)	-137	-128	-127	-130	-134	-134	-127	-134	-141	-132	-124
$\delta^{18}O$ (‰VSMOW)	-17.5	-16.2	-15.8	-16.8	-16.0	-16.0	-16.7	-17.0	-18.2	-16.3	-15.9
^3H (TU)		5.2±0.8		5.3±0.9							
$^3H/^3He$ (TU)											
$^3H/^3He$ age (yr)											
^{14}C (pmC)		98.63±0.23		80.44±0.19							
CRA (yr BP)		55±20		1692±20							
$\delta^{13}C$ (‰VPDB)		-12.5		-16.4							

Table C.1 continued

Location	Highlands										
Water system	Anarchist Mountain										
Well ID	96 (2)	96 (3)	97 (1)	98 (1)	100a (1)	100b (1)	101a (1)	101b (1)	102 (1)	103 (1)	104 (1)
Elevation (masl)	772	772	1141	1139	761	761	762	762	1152	1082	1067
Well depth (masl)	635	635			731	755	634	756		972	
Screened material	Br	Br	Br	Br	Br	Br	Br	Br	Br	Br	Br
Aquifer No.	808	808	n/v	n/v	808	808	808	808	n/v	810	n/v
Date sampled	7/26/06	11/20/07	8/16/06	8/16/06	5/21/06	5/21/06	5/21/06	5/21/06	8/16/06	9/12/08	8/16/06
Field pH											
Field HCO_3											
pH											
Alkalinity ($CaCO_3$)											
HCO_3											
CO_3											
OH											
Cl											
NO_3 (N)											
SO_4											
Ca											
Fe											
Mg											
Mn											
K											
Na											
δ^2H (‰VSMOW)	-123	-134	-135	-135	-126	-127	-135	-136	-135	-144	-133
$\delta^{18}O$ (‰VSMOW)	-16.2	-17.1	-17.2	-17.1	-16.1	-15.9	-16.7	-17.0	-17.0	-18.2	-17.0
^3H (TU)											
$^3H/^3He$ (TU)											
$^3H/^3He$ age (yr)											
^{14}C (pmC)											
CRA (yr BP)											
$\delta^{13}C$ (‰VPDB)											

Table C.1 continued

Location	Highlands					
Water system	Anarchist Mountain		Mt. Baldy	Spring (Mt. Baldy)	Spring (Anarchist Mountain)	Spring (Anarchist Mountain)
Well ID	106 (1)	108 (1)	11 (1)			
Spring ID	106 (1)	108 (1)	11 (1)	12 (1)	81 (1)	82 (1)
Elevation (masl)	1088	1117	1739	1874	1148	1151
Well depth (masl)			1733	n/a	n/a	n/a
Screened material	Br	Br	Br	Br	Br	Br
Aquifer No.	n/v	n/v	n/v	n/v	n/v	n/v
Date sampled	8/16/06	8/16/06	9/12/08	9/12/08	9/12/08	9/12/08
Field pH						
Field HCO_3						
pH						
Alkalinity ($CaCO_3$)						
HCO_3						
CO_3						
OH						
Cl						
NO_3 (N)						
SO_4						
Ca						
Fe						
Mg						
Mn						
K						
Na						
δ^2H (‰VSMOW)	-136	-133	-132	-126	-138	-137
$\delta^{18}O$ (‰VSMOW)	-16.6	-16.4	-16.7	-15.6	-17.3	-17.0
^3H (TU)						
$^3H/^3He$ (TU)						
$^3H/^3He$ age (yr)						
^{14}C (pmC)						
CRA (yr BP)						
$\delta^{13}C$ (‰VPDB)						

Water levels measured at shallow groundwater wells in the Osoyoos area, BC, Canada, are provided in Table C.2.

Table C.2. Summary of manual water level measurements in masl at shallow groundwater wells in the valley bottom and benchlands of the Osoyoos area, British Columbia, Canada. Blank cell indicates water level not measured. Water levels measurements are not provided for well 43 as well casing was damaged prior to obtaining top of casing elevation.

Sample Date		9/25/04	7/02/05	7/05/05	9/02/05	2/14/06	4/01/06	4/19/06	4/26/06	5/03/06	5/24/06	6/03/06	6/05/06	7/25/06	9/26/06	2/16/07
System	ID															
North	26				290.12									289.8	290.7	
	27a					Dry		Dry	Dry		Dry			300.6	Dry	
	27c					299.6					299.3		299.3	300.0	300.1	
	28	317.9	318.1	318.6	318.7	317.3	316.7	315.9	315.5	316.5	318.6	318.4	318.7	318.2	316.6	315.2
	29a					316.4		315.4	315.2		316.9		316.9	317.1	316.0	315.3
	29b					304.5		304.0	304.0		303.9				304.6	
	30	314.6	313.5	313.5	313.8	313.9	313.7	313.5	313.5	313.4	313.4	313.6	313.6	318.0	314.0	313.5
	31b					316.2		315.8	315.7		316.0		316.0	316.8	317.0	315.8
	35					292.8	292.7	292.8	292.7	292.6	293.1	293.1		293.7	293.6	
	39	315.1	314.7		315.6	315.2	314.4	314.8	314.6	314.6	314.9	315.3	314.9	315.4	315.1	314.2
Central	42												282.0	282.7	282.3	
	44												274.5	274.2	274.2	
	54a	281.2		281.9		281.2		281.4	281.5		282.1			282.0	281.7	
	54b	281.2		281.9		281.2		281.4	281.5		282.1			282.0	281.7	
South	61	288.6		287.4		287.7		287.5	287.5		287.6			288.0	288.5	
	62a	288.5		287.4		287.7		287.5	287.5		287.5			287.9	288.4	
	62b	288.6		287.4		287.7		287.5	287.5		287.5			287.9	288.4	
	66a			300.6		299.8		299.7	299.7		300.2			300.8	301.2	
	66b	301.2		300.6		299.8		299.7	299.7		300.2			300.8	301.2	
	70			303.3		302.6		302.5	302.5		302.9			303.5	303.9	
	72a	301.8	301.2	301.2	301.7	300.7	300.7	300.6	300.6	300.6	300.9	301.0		301.3	301.8	
	72b	301.8	301.1	301.2	301.7	300.7	300.7	300.6	300.6	300.6	300.9	301.0		301.3	301.8	
	74a	301.1		300.7		300.3		300.2	300.2		300.4			300.8	301.2	
	74b			300.7		300.3		300.2	300.2		300.4			300.8	301.2	

Saturation indices for select mineral phases in groundwaters collected in the South Okanagan Basin, British Columbia, Canada, are provided in Table C.3.

Table C.3. Saturation indices (SI) for select mineral phases in groundwaters in the study area.

Water System	Well ID	Date Sampled	$SI_{CO2(g)}$	$SI_{Aragonite}$	$SI_{Calcite}$	$SI_{Dolomite}$	$SI_{Fe(OH)3}$	$SI_{Goethite}$	$SI_{Hematite}$	$SI_{Rhodochrosite}$
Upper Bench	38	5/17/06	-1.87	0.28	0.42	0.40	0.24	5.95	13.88	-2.27
	38	7/27/06	-1.95	0.42	0.57	0.63	1.20	6.91	15.81	-0.42
	38	9/29/06	-1.87	0.32	0.46	0.39	-0.21	5.50	12.99	-2.24
Shallow North	25	5/25/06	-2.13	0.30	0.45	0.83	0.70	6.41	14.81	-1.68
	25	9/26/06	-1.93	0.31	0.45	0.82	-0.14	5.57	13.12	-2.22
	26	10/5/06	-1.66	-0.08	0.07	-0.27	0.46	6.17	14.33	-2.22
	27a	8/17/06	-1.89	-0.15	-0.01	-0.52	0.12	5.83	13.65	-2.49
	27a	5/25/06	-1.88	0.18	0.33	0.59	1.03	6.74	15.47	-0.94
	27a	7/26/06	-1.76	0.07	0.22	0.37	1.05	6.76	15.50	-0.52
	27a	9/28/06	-1.70	0.09	0.23	0.43	0.41	6.12	14.22	-1.15
	28	5/25/06	-1.61	0.07	0.22	0.21	0.17	5.88	13.74	-1.98
	28	7/26/06	-1.55	-0.06	0.09	-0.09	0.12	5.83	13.65	-1.12
	28	9/28/06	-1.50	-0.15	-0.01	-0.17	0.02	5.73	13.43	-2.58
	29a	5/24/06	-1.84	0.15	0.30	0.51	1.71	7.42	16.83	1.12
	29a	7/26/06	-1.79	0.11	0.25	0.46	-0.02	5.69	13.36	0.86
	29a	9/27/06	-1.72	-0.02	0.13	0.29	0.66	6.37	14.72	0.73
	29a	2/16/07	-1.71	0.13	0.27	0.49	0.95	6.66	15.30	0.77
	29b	7/29/06	-2.33	0.28	0.42	1.12	1.23	6.94	15.86	0.85
	29b	9/30/06	-2.26	0.19	0.33	0.97	0.69	6.40	14.78	0.55
	30	5/25/06	-1.63	0.11	0.26	0.16	-0.43	5.28	12.54	-2.00
	30	5/25/06	-1.63	0.11	0.26	0.16	0.52	6.23	14.44	-2.48
	30	7/26/06	-1.55	0.11	0.25	0.16	-0.37	5.34	12.67	-2.00
	30	7/26/06	-1.55	0.11	0.25	0.17	-0.14	5.57	13.12	-1.28
	30	9/27/06	-1.56	-0.06	0.09	-0.08	-0.28	5.43	12.84	-2.52
	30	9/27/06	-1.56	-0.01	0.14	-0.02	-0.28	5.43	12.84	-2.52
	31b	5/24/06	-1.69	0.03	0.18	0.15	0.42	6.13	14.24	-0.70
	31b	7/26/06	-1.63	-0.03	0.12	0.04	-0.75	4.96	11.91	-1.53
	31b	9/27/06	-1.63	0.00	0.15	0.11	-0.73	4.98	11.95	-1.77
	31b	2/16/07	-1.82	0.22	0.37	0.50	-0.30	5.41	12.81	-2.29
	32	6/3/06	-2.28	-0.18	-0.03	-0.34	1.39	7.10	16.19	-1.16
	32	9/30/06	-2.06	-0.22	-0.07	-0.44	0.17	5.88	13.75	-2.49
	35	5/27/06	-1.89	0.14	0.29	0.19	0.16	5.87	13.73	1.06
	35	7/27/06	-1.50	-0.11	0.04	-0.30	0.06	5.77	13.53	1.15
	35	9/28/06	-1.35	-0.04	0.10	-0.15	-0.14	5.57	13.12	1.28
	37	5/17/06	-1.90	0.03	0.18	-0.08	0.48	6.19	14.36	-1.34
	37	9/28/06	-1.95	0.13	0.28	0.14	-0.28	5.43	12.84	-2.39
	39	5/25/06	-1.92	0.07	0.22	0.14	0.77	6.48	14.94	-1.27
	39	7/27/06	-1.72	-0.11	0.03	-0.35	-0.24	5.47	12.92	-1.58
	39	9/28/06	-1.72	-0.18	-0.03	-0.47	-0.25	5.46	12.90	-1.84
	39	2/16/07	-1.99	0.07	0.22	0.14	0.85	6.56	15.11	-2.31

Table C.3 continued

Water System	Well ID	Date Sampled	$SI_{CO2(g)}$	$SI_{Aragonite}$	$SI_{Calcite}$	$SI_{Dolomite}$	$SI_{Fe(OH)3}$	$SI_{Goethite}$	$SI_{Hematite}$	$SI_{Rhodochrosite}$
Shallow Central	43	6/13/06	-1.49	0.01	0.16	-0.06	-0.75	4.96	11.90	-2.57
	43	9/26/06	-1.74	0.20	0.34	0.40	-0.43	5.28	12.55	-1.56
	44	9/26/06	-1.81	0.35	0.50	0.76	-0.27	5.44	12.86	-1.96
	46	6/13/06	-1.78	-0.05	0.10	-0.14	-0.45	5.26	12.51	-2.38
	52	6/2/06	-1.53	-0.09	0.06	-0.38	-1.02	4.69	11.36	-2.58
	52	10/4/06	-1.94	0.17	0.31	0.29	-0.14	5.57	13.12	-2.22
	54a	5/25/06	-1.78	0.04	0.19	0.20	-0.18	5.53	13.04	-2.42
	54a	9/26/06	-1.43	-0.19	-0.04	-0.26	-0.82	4.89	11.76	-2.20
	54b	5/25/06	-1.78	0.02	0.16	0.14	-0.50	5.21	12.40	-1.53
	54b	9/26/06	-1.43	-0.19	-0.04	-0.26	-1.30	4.41	10.81	-2.68
	57	5/17/06	-1.77	-0.25	-0.10	-0.51	-0.72	4.99	11.97	-1.67
	57	9/28/06	-1.66	0.05	0.20	-0.07	-0.41	5.30	12.58	-2.18
Shallow South	61	5/26/06	-1.87	0.15	0.30	0.09	-0.33	5.38	12.74	-2.36
	61	9/29/06	-1.76	-0.09	0.06	-0.37	-0.67	5.04	12.07	-2.53
	62a	5/26/06	-1.82	0.07	0.22	0.03	-0.11	5.60	13.18	-1.61
	62a	9/29/06	-1.77	-0.14	0.00	-0.44	-0.66	5.05	12.08	-2.06
	62b	5/26/06	-2.07	0.09	0.24	0.33	1.45	7.16	16.30	-0.01
	62b	9/29/06	-1.83	-0.17	-0.02	-0.19	1.91	7.62	17.22	-0.15
	66a	5/26/06	-1.82	0.04	0.19	-0.17	-0.51	5.20	12.38	-2.16
	66a	9/26/06	-1.60	-0.04	0.11	-0.29	-0.89	4.82	11.62	-2.08
	66a	9/26/06	-1.60	-0.03	0.12	-0.28	-0.90	4.81	11.61	-2.08
	66b	5/26/06	-1.79	0.05	0.20	-0.13	-0.51	5.20	12.38	-2.44
	66b	9/26/06	-1.59	-0.07	0.08	-0.35	-0.94	4.77	11.52	-2.58
	70	5/26/06	-1.90	0.00	0.15	-0.23	0.04	5.75	13.48	-1.69
	70	9/26/06	-1.55	-0.05	0.09	-0.32	-1.07	4.64	11.27	-2.64
	72a	5/26/06	-2.05	0.04	0.19	0.06	0.33	6.04	14.06	-2.01
	72a	9/27/06	-1.79	-0.14	0.01	-0.38	-0.58	5.13	12.24	-2.49
	72b	5/26/06	-2.08	-0.04	0.11	-0.15	0.78	6.49	14.97	-2.36
	72b	9/27/06	-1.74	-0.22	-0.07	-0.56	0.06	5.77	13.52	-1.77
	74a	5/26/06	-1.91	0.06	0.20	-0.05	-0.39	5.32	12.63	-2.15
	74a	9/29/06	-1.69	-0.10	0.04	-0.37	-0.53	5.18	12.34	-2.60
	74b	5/26/06	-1.87	0.13	0.28	0.11	-0.08	5.63	13.25	-2.10
	74b	5/26/06	-1.87	0.14	0.29	0.12	-0.08	5.63	13.25	-2.10
	74b	9/26/06	-1.64	-0.18	-0.03	-0.51	-0.38	5.33	12.64	-2.36

APPENDIX D
NITRATE AND ISOTOPES OF NITRATE DATA

Chemical and isotopic composition of groundwaters, including nitrate concentrations and isotopic composition of nitrate, collected in the Osoyoos area, British Columbia, Canada, are provided in Table D.1.

Table D.1. Chemical and isotopic data for groundwater samples collected in the Osoyoos area. Historical NO_3-N concentrations from observation wells 28, 30, 39, 72a and 72b reported as NO_3 + NO_2 (where NO_2 is negligible). Blank cell indicates parameter not analyzed. Red DO reading discarded as value was inferred to represent stagnant well water, not aquifer water.

Well ID	*Date sampled (m/dd/yy)*	*DO (mg/l)*	*NO_3-N (mg/l)*	*NO_2-N (mg/l)*	*NH_3 (mg/l)*	*TKN (mg/l)*	*Cl (mg/l)*	*$\delta^{15}N_{NO3}$ (‰)*	*$\delta^{18}O_{NO3}$ (‰)*	*$\delta^{2}D_{H2O}$ (‰)*	*$\delta^{18}O_{H2O}$ (‰)*	*$\delta^{18}O_{DO}$ (‰)*	*Predicted $\delta^{18}O_{NO3}$ (‰)*
North													
24	6/2/06		0				6			-107	-12.8		
	8/2/06		0				6			-108	-11.1		
	9/30/06		0.2				7			-106	-11.2		
	4/23/08									-112	-12.5		
25	5/25/06		5.7				28	5.0	-3.4	-103	-10.9		
	7/28/06									-114	-13.0		
	9/26/06		0.5				49			-110	-12.9		
26	8/24/88				0.005	0.61	4.8						
	10/30/88				0.005	0.52	4.8						
	8/2/06									-106	-11.7		
	5/10/06		1.7				10			-104	-10.8		
27a	8/17/06	7.90	1.1				7	3.8	-5.9	-106	-11.8		
27c	2/14/06	2.30	6.5				4	8.00	8.11	-108	-12.1		
	5/24/06	1.74	5.1				5			-108	-11.7	23.1	-0.1
	7/26/06	0.55	5.0				7	9.0	8.3	-113	-11.3		
	9/28/06	0.64	4.3				5			-106	-12.2	22.9	-0.5

Table D.1 continued

Well ID	*Date sampled (m/dd/yy)*	*DO (mg/l)*	*NO_3-N (mg/l)*	*NO_2-N (mg/l)*	*NH_3 (mg/l)*	*TKN (mg/l)*	*Cl (mg/l)*	*$\delta^{15}N_{NO3}$ (‰)*	*$\delta^{18}O_{NO3}$ (‰)*	*$\delta^{2}D_{H2O}$ (‰)*	*$\delta^{18}O_{H2O}$ (‰)*	*$\delta^{18}O_{DO}$ (‰)*	*Predicted $\delta^{18}O_{NO3}$ (‰)*
28	8/24/88		3.1		0.005	0.68	10.1						
	10/30/88		2.8		0.005	0.36	10.1						
	1/8/90		1.7		0.074	0.50	11.0						
	8/13/90		1.3	0.006	0.022	0.46	11.7						
	9/24/04		10.5				17			-106	-12.1		
	2/14/06	4.67	9.6				16	7.18	1.09	-102	-11.7		
	5/25/06	6.42	9.9				31			-103	-11.6	21.9	-0.4
	7/26/06	4.48	10.2				22			-108	-10.5		
	9/28/06	2.60	9.3				20			-102	-11.7	23.9	0.2
29a	2/14/06	1.51	5.0				25	11.21	5.66	-104	-11.9	23.2	-0.2
	5/24/06	0.49	5.0				19			-107	-11.5		
	7/26/06	0.10	7.5				13			-102	-11.2		
	9/27/06	0.18	7.7				13			-103	-11.8	21.5	-0.7
	2/16/07	0.60	2.9				14			-104	-12.2		
29b	7/29/06		0.4				10			-117	-11.8		
	9/30/06		1.4				11			-110	-12.6		
30	8/24/88		7.1		0.005	0.81	9.1						
	10/30/88		6.7		0.231	0.97	9.1						
	7/25/89		6.4	0.005	0.007	0.60	9.1						
	8/1/90		6.3		0.005	0.59	8.9						
	8/13/91		5.1	0.062	0.173	0.65	8.7						
	9/24/04	2.36	7.3				16			-107	-12.1		
	2/14/06	3.67	12.8				17	5.62	2.14	-104	-11.5	23.0	0.03
	5/25/06	2.45	15.0				20			-103	-11.0	23.6	0.5
	5/25/06		15.0				19			-100	-11.9		
	7/26/06	2.84	8.1				16			-107	-10.2		
	7/26/06		7.5				14						
	9/27/06	4.22	14.7				15			-100	-11.3	23.5	0.3
	9/27/06		12.9				14						
31a	Dry												

Table D.1 continued

Well ID	*Date sampled (m/dd/yy)*	*DO (mg/l)*	*NO_3-N (mg/l)*	*NO_2-N (mg/l)*	*NH_3 (mg/l)*	*TKN (mg/l)*	*Cl (mg/l)*	*$\delta^{15}N_{NO3}$ (‰)*	*$\delta^{18}O_{NO3}$ (‰)*	*$\delta^{2}D_{H2O}$ (‰)*	*$\delta^{18}O_{H2O}$ (‰)*	*$\delta^{18}O_{DO}$ (‰)*	*Predicted $\delta^{18}O_{NO3}$ (‰)*
31b	2/14/06	3.48	6.4				13	4.20	3.64	-104	-11.5	23.3	0.1
	5/24/06	3.39	6.9				14			-104	-11.2		
	7/26/06	3.30	8.6				14			-95	-10.6		
	9/27/06	3.25	9.7				14			-101	-11.6	22.9	-0.1
	2/16/07	8.77	10.0				12			-101	-11.8		
32	6/2/06		3.2				42			-102	-12.5		
	9/30/06		4.3				55			-103	-10.8		
34a, 34b	Dry												
35	8/24/88		0.4		0.016	0.42	4.8						
	10/30/88		0.4		0.005	0.23	4.2						
	7/25/89		0.5	0.005	0.006	0.17	4.3						
	8/1/90		0.5		0.005	0.18	4.4						
	8/13/91		0.4	0.005	0.005	0.17	4.3						
	2/16/06		6.0				29	15.51	1.20	-108	-12.7		
	2/16/06		5.9				28						
	5/27/06	**5.58**	6.8				25	9.3	4.6	-104	-12.0		
	7/27/06	0.90	3.8				22			-106	-10.4		
	9/28/06	1.20	0.3				25			-101	-11.7		
37	5/17/06		14.0				25			-101	-11.4		
	7/25/06									-106	-11.2		
	9/28/06		10.4				28			-102	-11.7		
38	5/17/06		0.1				58			-121	-16.1		
	7/27/06		0				31			-124	-15.5		
	9/29/06		0				22			-121	-15.3		
39	8/24/88		0.4		0.005	0.51	4.9						
	10/30/88		0.4		0.005	0.57	5.0						
	7/26/89		0.7	0.005	0.005	0.67	6.0						
	8/1/90		0.4		0.005	0.51	6.6						
	8/13/91		0.4	0.005	0.005	0.45	7.3						
	9/24/04	6.04	5.8				13			-105	-12.1		
	2/16/06		4.2				12	3.06	-0.03	-93	-11.8		

Table D.1 continued

Well ID	*Date sampled (m/dd/yy)*	*DO (mg/l)*	*NO_3-N (mg/l)*	*NO_2-N (mg/l)*	*NH_3 (mg/l)*	*Cl (mg/l)*	*$\delta^{15}N_{NO3}$ (‰)*	*$\delta^{18}O_{NO3}$ (‰)*	*$\delta^{2}D_{H2O}$ (‰)*	*$\delta^{18}O_{H2O}$ (‰)*	*$\delta^{18}O_{DO}$ (‰)*	*Predicted $\delta^{18}O_{NO3}$ (‰)*
39 cont'd	5/25/06	6.34	5.0			12			-104	-11.1	23.6	0.4
	7/27/06	5.99	6.3			14			-103	-10.3		
	9/28/06	5.57	0.3			9			-104	-12.1	18.3	-2.0
	2/16/07	2.31	4.1			11						
Central												
42	13/6/06	6.26	5.2			7			-98		23.5	
	7/27/06	10.20							-108	-12.1		
	9/30/06	9.17	6.8			6	6.4	-3.7	-99	-11.2	24.1	0.6
43	13/6/06	7.21	2.5			10			-98		20.2	
	7/27/06	9.06							-107	-12.2		
	9/30/06	7.09	3.4			6			-101	-11.4	24.0	0.4
44	13/6/06	8.17	7.3			6			-104		23.6	
	7/27/06	5.06							-104	-11.1		
	9/30/06	3.00	2.7			6			-101	-11.1	23.6	0.5
46	13/6/06		6.1			6			-103			
	7/27/06								-105	-11.5		
52	6/2/06		6.1			23			-102	-12.1		
	7/27/06								-103	-11.7		
	10/4/06		7.3			20			-102	-11.6		
54a	9/24/04	6.00	6.6			17			-105	-11.7		
	2/16/06		0.9			15	6.23	-1.65	-103	-11.7		
	5/25/06	9.82	6.2			16			-101	-12.0	22.3	-0.6
	7/27/06	8.32							-104	-11.7		
	9/26/06	6.23	7.5			16	5.8	2.3	-102	-11.5	22.8	-0.05
54b	2/28/06		9.0			14			-104	-11.8		
	5/25/06	9.74	5.3			15			-100	-12.1	23.1	-0.4
	7/27/06	7.93							-103	-11.5		
	9/26/06	6.22	7.2			17			-102	-11.6	23.4	0.1
57	2/17/06		2.3			10	5.05	-2.66	-98	-10.8		
	5/17/06		3.8			13	5.8	-4.9	-97	-10.5		
	7/26/06								-102	-11.0		
	9/28/06		2.2			9			-100	-11.2		

Table D.1 continued

Well ID	*Date sampled (m/dd/yy)*	*DO (mg/l)*	*NO_3-N (mg/l)*	*NO_2-N (mg/l)*	*NH_3 (mg/l)*	*Cl (mg/l)*	*$\delta^{15}N_{NO3}$ (‰)*	*$\delta^{18}O_{NO3}$ (‰)*	*$\delta^{2}D_{H2O}$ (‰)*	*$\delta^{18}O_{H2O}$ (‰)*	*$\delta^{18}O_{DO}$ (‰)*	*Predicted $\delta^{18}O_{NO3}$ (‰)*
South												
61	9/24/04	5.00	4.5			50			-105	-12.3		
	2/15/06	6.94	4.0			18	4.46	2.55	-104	-11.7	18.0	-1.8
	5/26/06	5.46	5.5			19	4.0	2.0	-103	-11.5	22.9	-0.01
	7/28/06	5.38							-105	-10.8		
	9/29/06	6.54	4.3			42			-105	-12.6	20.7	-1.5
62a	9/24/04	1.94	3.2			47			-99	-10.2		
	2/15/06	3.07	3.3			23	7.46	2.10	-103	-11.8	21.3	-0.7
	5/26/06	1.84	3.7			28	6.3	3.3	-98	-10.7	24.0	0.9
	7/28/06	0.89							-96	-9.3		
	9/29/06	0.57	2.5			34			-96	-10.7	22.8	0.5
62b	9/24/04	0.16	0.7			31			-88	-8.2		
	2/15/06	0.60	0			26	9.90	-1.51	-90	-9.0	22.9	1.6
	5/26/06	0.04	0.2			34	5.0	6.8	-87	-6.8	24.2	3.5
	7/28/06	0.12							-89	-7.6		
	9/29/06	0.09	0.1			31			-88	-8.6	23.5	2.1
66a	2/17/06		7.0			20	3.86	-2.94	-101	-11.2		
	5/26/06	6.33	6.5			22			-101	-9.6	22.9	1.3
	7/28/06	5.57							-103	-11.1		
	9/29/06	7.96	9.5			27			-103	-11.6	23.5	0.1
	9/29/06		11.1			25						
66b	9/24/04	7.82	11.9			22			-106	-11.8		
	2/17/06		6.0			17	4.66	-2.00	-101	-11.2		
	5/26/06	6.63	5.8			22			-99	-11.4	20.2	-0.9
	7/28/06	7.35							-102	-11.6		
	9/29/06	8.33	9.3			25	4.8	-2.3	-102	-11.7	23.9	0.2
70	9/24/04	7.52	14.7			17	5.16	-2.19	-101	-11.7		
	2/16/06	7.50	10.3			28			-105	-12.2		
	2/16/06		10.2			29						
	5/26/06	7.54	10.0			26			-101	-10.9	23.1	0.4
	7/28/06	7.68							-107	-11.7		
	9/26/06	8.70	24.4			31	6.9	0.9	-104	-11.8	23.1	-0.1

Table D.1 continued

Well ID	*Date sampled (m/dd/yy)*	*DO (mg/l)*	*NO_3-N (mg/l)*	*NO_2-N (mg/l)*	*NH_3 (mg/l)*	*Cl (mg/l)*	*$\delta^{15}N_{NO3}$ (‰)*	*$\delta^{18}O_{NO3}$ (‰)*	*$\delta^{2}D_{H2O}$ (‰)*	*$\delta^{18}O_{H2O}$ (‰)*	*$\delta^{18}O_{DO}$ (‰)*	*Predicted $\delta^{18}O_{NO3}$ (‰)*
72a	8/24/88		2.7									
	10/30/88		2.7									
	7/25/89		3.2									
	8/1/90		1.7									
	8/13/91		2.1									
	8/31/93		2.6									
	8/31/00		0									
	9/24/04	6.84	3.1			11			-100	-11.4		
	2/15/06	6.70	4.6			8	2.82	6.43	-103	-11.2		
	5/26/06		2.6			10			-103	-11.2	23.2	0.3
	7/28/06	6.15							-99	-10.6		
	9/27/06	4.34	1.0			9			-99	-11.2	23.4	0.4
72b	8/24/88		0									
	10/30/88		4.0									
	9/24/04	6.18	2.5			12			-100	-11.3		
	5/26/06	6.07	1.9			10	1.8	-0.4	-105	-11.6	19.3	-1.3
	7/28/06	6.47							-101	-10.9		
	9/27/06	7.57	0.9			17			-99	-11.2	22.4	-0.03
74a	9/24/04	7.44	13.4			33			-105	-11.7		
	2/16/06		10.4			20	3.87	7.94	-100	-11.5		
	5/26/06	8.38	16.0			28			-103	-11.4	22.1	-0.3
	7/28/06	8.25							-108	-11.4		
	9/26/06	7.74	15.8			34	4.5	10.7	-103	-11.5	24.4	0.5
74b	2/16/06	8.30	10.3			19	4.36	7.88	-102	-11.7		
	5/26/06	7.92	15.0			30			-101	-11.4	22	-0.3
	5/26/06		15.0			30						
	7/28/06	7.22							-108	-11.3		
	9/26/06	6.76	15.6			34			-102	-11.5	22.9	-0.03
Irrigation	5/31/06								-106	-12.8		
User	7/26/06								-108	-12.1		
	9/28/06		0			7			-102	-10.9		

The δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values of silt porewater are provided in Table D.2.

Table D.2. δ^2H_{H2O} and $\delta^{18}O_{H2O}$ values of silt porewater. Red values discarded as samples may have been affected by evaporation during storage.

Sample ID	*Depth (mbgs)*	*δ^2H_{H2O} (‰)*	*$\delta^{18}O_{H2O}$ (‰)*
SB	1.52	**-98.2**	**-11.35**
SC	1.91	-104.6	-12.30
SD	2.00	-104.3	-12.37
SE	2.10	-105.4	-12.34
SF	2.20	-104.8	-12.34
SI	2.29	-105.8	-12.30
SJ	2.39	-104.0	-12.15
SL	2.58	-103.8	-12.10
SK	2.67	-103.9	-12.06
SO	2.77	-103.5	-11.94
SP	2.86	-102.2	-11.98
SQ	2.96	-102.7	-11.99
SS	3.05	-102.4	-11.88
ST	3.14	-102.3	-11.90
SU	3.24	-101.8	-12.00
SV	3.34	-101.9	-11.76
SY	3.43	-101.9	-11.68
SZ	3.53	-102.2	-11.91
SAA	3.62	-101.7	-11.93
SAB	3.72	-101.6	-11.82
SAE	3.81	-101.4	-11.62
SAF	3.85	-101.0	-11.82
SAG	3.91	-101.0	-11.70
SAH	3.98	-100.8	-11.58
SAK	4.04	-101.1	-11.63
SAL	4.14	-100.6	-11.64
SAM	4.23	-100.7	-11.49
SAN	4.40	-101.1	-11.70
SAQ	4.57	-101.2	-11.69
SAR	4.67	-100.8	-11.62
SAS	4.76	-100.8	-11.65
SAT	4.86	-101.0	-11.62
SAW	4.95	-101.7	-11.63
SAX	5.05	-101.0	-11.66
SAY	5.14	-101.4	-11.82
SAZ	5.24	-101.5	-11.76
SBC	5.34	-101.2	-11.74
SBD	5.44	-100.9	-11.71
SBE	5.53	-100.4	-11.62
SBF	5.63	-101.4	-11.73
SBI	5.72	-101.1	-11.72
SBJ	5.82	-101.4	-11.70
SBK	5.91	-101.1	-11.83
SBL	6.00	-101.9	-11.86
SBO	6.10	-102.2	-11.81
SBP	6.20	-103.3	-11.88
SBQ	6.29	-102.8	-11.92
SBR	6.39	-101.5	-11.77
SBV	6.58	-102.6	-11.86

Table D.2 Continued.

Sample ID	*Depth (mbgs)*	$\delta^{2}H_{H2O}$ (‰)	$\delta^{18}O_{H2O}$ (‰)
SBW	6.67	-102.5	-11.82
SBX	6.77	-102.0	-11.88
SCA	6.86	-102.0	-11.96
SCB	6.96	-102.3	-11.79
SCC	7.05	-103.1	-12.04
SCD	7.15	-102.3	-12.04
SCG	7.24	-102.2	-11.92
SCH	7.34	-102.7	-11.97
SCI	7.53	-103.0	-12.03
SCL	7.62	-103.2	-11.95
SCM	7.72	-103.1	-11.93
SCN	7.81	-103.0	-11.94
SCR	7.91	-104.0	-11.91
SCO	8.00	-103.2	-12.03
SCS	8.10	-103.1	-11.99
SCT	8.19	-102.8	-11.90
SCU	8.29	-103.6	-11.95
SCX	8.38	-103.3	-11.96
SCY	8.48	-102.9	-12.03
SCZ	8.57	-103.4	-12.09
SDA	8.67	-103.4	-11.90
SDD	8.77	-103.4	-12.04
SDE	8.87	-104.2	-12.03
SDF	8.96	-102.9	-12.04
SDG	9.06	-102.1	-11.73
SDJ	9.15	-102.0	-11.58
SDK	9.53	-102.1	-11.95
SDM	9.91	-101.5	-11.75
SDN	10.29	-100.8	-11.50
SDP	10.67	-101.5	-11.57
SDQ	11.05	-101.4	-11.79
SDS	11.43	-101.1	-11.77
SDT	11.81	-100.2	-11.67
SDV	12.20	-100.9	-11.64
SDW	12.58	-101.7	-11.94
SDY	12.96	-101.0	-11.78
SDZ	13.34	-100.4	-11.55
SEB	13.72	-101.2	-11.85
SEC	14.10	-101.4	-11.92
SEE	14.48	-101.1	-11.64
SEF	14.86	-100.8	-11.73
SA	15.24	-101.0	-11.53

Chemical and isotopic composition of agricultural drainage, including nitrate concentrations and isotopic composition of nitrate, collected in the Osoyoos area, British Columbia, Canada, are provided in Tables D.3.

Table D.3. Chemical and isotopic data for agricultural drainage system waters. Concentrations as noted. Blank cell indicates parameter not analyzed. Red values discarded as δ^2H_{H2O} or $\delta^{18}O_{H2O}$ may have been affected by evaporation during storage.

ADS	*Date sampled (m/dd/yy)*	*Flow Rate (m/s)*	*NO_3-N (mg/l)*	*$\delta^{15}N_{NO3}$ (‰)*	*$\delta^{18}O_{NO3}$ (‰)*	*δ^2H_{H2O} (‰)*	*$\delta^{18}O_{H2O}$ (‰)*
ADS O2							
R1	2/17/06		6.6	6.85	-0.4	**-95**	**-11.6**
O2	5/3/06	1	7.0			-101	-11.0
	5/17/06	5	8.0	7.0	2.4	**-101**	**-7.8**
	6/3/06	5	6.6			-101	-13.3
	6/13/06	5	7.5				
	7/7/06	6	7.1			-102	-11.6
	7/18/06	6	6.8			-105	-11.7
	8/2/06	10	6.3			-105	-11.4
	8/17/06	13	5.4			-104	-11.6
	9/8/06	12	6.1			-103	-11.6
	9/22/06	18	4.9			-101	-11.5
	10/4/06	18	5.4			-101	-11.4
	10/20/06	18	3.4	4.4	-1.4	-99	-11.2
	11/2/06	9	5.9			-100	-11.3
	12/9/06		8.3			-100	-11.5
	1/22/07	10	1.4			-101	-11.6
	2/15/07	6	7.5			-101	-11.6
	3/24/07	4	6.3			-101	-11.8
	5/5/07	3	5.4			-102	-12.0
	6/16/07	10	6.4			-101	-11.9
	7/15/07	10	6.6			-100	-11.7
	8/18/07	18	6.6			-101	-11.8
	10/5/07	8	5.5			-101	-11.6
	11/17/07	5	7.0			-99	-11.5
	12/29/07	3	7.5			-100	-11.4
	1/27/08	3	8.0			-106	-11.5
	3/8/08	3	8.2			-106	-11.8
	4/24/08	4	9.3			-107	-12.1
EC	3/12/97		18.34	6.9	3.1	-104.5	-12.1
	4/26/97		11.33	6.2	1.1	-104.7	-12.2
	5/23/97		13.50	6.5	1.9		
	6/21/97		13.54	6.8	2.5	-105.6	-12.5
	7/25/97		10.76	6.0	2.2		
	8/23/97		9.73	6.3	2.1	-105.3	-12.4
	9/28/97		9.83	6.1	1.7		
	10/18/97		14.09	6.4	3.1	-103.6	-12.1
	11/16/97		14.07	6.4	1.5		
	12/20/97		14.17	6.2	1.4		
	1/17/98		13.84	6.3	1.7	-104.5	-12.2
	2/15/98		12.03	6.2	1.4		
	3/2/98		12.05	6.2	1.3		
	4/14/98		11.48	5.4	1.6	-103.2	-11.9
	5/1/98		15.90	6.0	1.7	-102.9	-11.9
	6/1/98		7.94	5.5	3.1	-104.2	-12.4
	7/1/98		7.95	5.4	2.4		

Table D.3 continued

ADS	*Date sampled (m/dd/yy)*	*Flow Rate (m/s)*	*NO_3-N (mg/l)*	*$\delta^{15}N_{NO3}$ (‰)*	*$\delta^{18}O_{NO3}$ (‰)*	*$\delta^{2}H_{H2O}$ (‰)*	*$\delta^{18}O_{H2O}$ (‰)*
EC	8/1/98		7.99	5.3	2.6		
	9/1/98		7.86	5.6	2.5	-104.6	-12.3
	10/1/98		7.94	5.4	2.3		
	11/1/98		9.37	5.3	3.2		
	12/1/98		9.45	5.1	2.8		
	1/1/99		12.39	5.5	3.6	-104.9	-12.2
	2/1/99		12.23	5.7	3.3		
	3/31/99		9.70	5.5	2.2		
	4/15/99		9.26	5.5	2.4	-104.4	-12.3
	5/3/99		10.70	5.5	3.1	-103.5	-12.3
	5/22/99		7.28	4.1	1.4		
	5/31/99		7.83	5.5	1.1		
	6/29/99		6.67	5.4	1.3		
	7/30/99		6.45	4.9	0.9	-104.6	-12.4
	8/31/99		5.15	4.7	1.6		
	9/15/99		5.18	4.7	0.6		
	10/4/99		4.85	5.0	0.7		
	10/30/99		5.14	4.8	1.8		
	11/1/99		4.82	5.0	0.5	-104.5	-12.2
	12/2/99		5.96	4.9	0.8		
	12/15/99		6.54	5.6	1.6		
	1/5/00		6.31	5.4	1.9		
	1/15/00		8.71	6.0	3.1	-104.2	-12.2
	1/27/00		6.41	5.4	1.6	-103.6	-12.3
	2/15/00		7.67	5.9	2.1	-104.0	-12.3
	3/15/00		5.06	5.2	0.0	-104.9	-12.4
	4/15/00		5.04	5.2	-0.8		
	4/26/00		5.38	5.1	-0.5		
	5/15/00		6.04	5.9	0.8		
	6/15/00		6.62	5.9	1.7	-103.3	-12.3
	7/15/00		6.57	5.9	1.9		
	8/15/00		4.26	5.3	1.3	-102.5	-12.0
	9/15/00		4.28	5.3	1.3		
	10/15/00		4.22	5.8	1.3		
	11/6/00		4.49	5.5	1.1		
	12/19/00		4.57	5.8	1.1		
	1/30/01		4.32	6.4	0.2	-104.0	-12.0
	2/15/01		4.29	5.8	-0.3		
	3/26/01		3.69	7.5	-0.8	-105.8	-12.6
	4/30/01		6.99	7.5	1.8	-102.8	-12.1
	5/15/01		7.00	7.3	2.4		
	6/10/01		7.01	7.3	1.8		
	8/26/01		4.74	6.3	1.5	-101.6	-11.8
	9/15/01		4.73	6.3	1.6		
	10/20/01		4.75	4.6	3.2		
	11/19/01		5.16	4.5	2.5		
	1/1/02		7.63	5.0	1.9	-101.4	-11.7
	2/1/02		7.68	5.0	2.8		
	3/1/02		7.75	5.2	2.6		
	4/1/02		6.83	4.4	2.6		
	5/1/02		6.71	4.5	2.1		
	6/1/02		6.75	5.1	2.8	-102.3	-11.7
	7/1/02		5.87	5.3	2.7		
	8/1/02		5.90	4.9	2.7		
	9/1/02		5.95	4.7	3.3		
	10/1/02		4.67	4.4	1.9	-101.7	-11.6
	11/1/02		4.74	4.4	1.9		
	8/2/06	9	6.4	5.6	0.7	-105	-11.8

Table D.3 continued

ADS	*Date sampled (m/dd/yy)*	*Flow Rate (m/s)*	*NO_3-N (mg/l)*	*$\delta^{15}N_{NO3}$ (‰)*	*$\delta^{18}O_{NO3}$ (‰)*	*$\delta^{2}H_{H2O}$ (‰)*	*$\delta^{18}O_{H2O}$ (‰)*
EC	8/17/06	11	5.8			-104	-11.8
	9/8/06	12	5.4			-105	-11.1
	9/22/06	11	4.6			-101	-11.3
	10/4/06	22	5.1			-101	-11.2
	10/20/06	22	3.6	4.0	-1.4	-100	-10.5
	11/2/06	12	4.6			-101	-11.4
	12/9/06		5.8			-99	-11.7
	1/22/07	3	1.5			-99	-11.3
	2/15/07	3	9.2			-101	-11.8
	3/24/07	3	7.2			-101	-11.6
	5/5/07	3	6.0			-102	-12.0
	6/16/07	4	6.3			-101	-12.0
	7/15/07	10	6.3			-101	-11.8
	8/18/07	18	6.2			-101	-11.9
	10/5/07	4	7.3			-99	-11.6
	11/17/07	5	7.4			-101	-11.7
	12/29/07	2	8.2			-99	-11.5
	1/27/08	3	8.1			-107	-11.7
	3/8/08	2	9.3			-108	-11.9
	4/24/08	3	9.9			-109	-12.1
148th	5/17/06	1					
	9/22/06	2	7.9			-102	-11.2
	10/4/06	2	7.9	4.8	2.3	-100	-11.4
	10/20/06	2	6.3			-104	-10.4
	11/2/06	2	8.1			-102	-11.6
	1/22/07	1				-100	-11.5
	2/15/07	1	8.4			-102	-11.8
	3/24/07	1	7.2			-100	-11.6
	5/5/07	1	6.1			-101	-11.9
	6/16/07	2	7.0			-103	-11.9
	7/15/07	2	8.5			-102	-12.1
	8/18/07	2	6.8			-100	-11.5
	10/5/07	2	6.3			-100	-11.5
	11/17/07	2	6.9			-101	-11.6
	12/29/07	1	6.7			-100	-11.4
	1/27/08	1	7.0			-106	-11.7
	3/8/08	1	7.3			-108	-12.2
	4/24/08	1	7.1			-109	-12.5
PH	7/18/06		15			-106	-11.3
	8/17/06		12			-106	-11.8
	9/8/06		12			-105	-11.7
	9/22/06		12			-103	-11.5
	10/5/06		14	7.2	2.9	-102	-11.4
PHN	10/5/06		20	6.8	3.0	-102	-11.5
PHS	8/17/06	0.3	4.7			-105	-11.7
	9/8/06	0.2	5.4			-104	-11.8
	9/22/06	0.4	5.2			-102	-11.2
	10/5/06	0.4	5.6	4.0	-1.3	-100	-11.5
ADS O3							
O3	2/16/06		5.0			-102	-11.2
	5/3/06	1	7.2			-101	-11.0
	5/17/06		5.9	6.3	9.4	-101	-12.3
	6/3/06	0.2	3.6			-99	-11.7
	6/13/06		4.8				
	7/7/06	0.01	2.6			**-92**	**-9.7**
	7/18/06	1	1	7.0	11.1	-102	-11.1
	8/2/06	1	1.8			-98	-10.1

Table D.3 continued

ADS	*Date sampled (m/dd/yy)*	*Flow Rate (m/s)*	*NO_3-N (mg/l)*	*$\delta^{15}N_{NO3}$ (‰)*	*$\delta^{18}O_{NO3}$ (‰)*	*$\delta^{2}H_{H2O}$ (‰)*	*$\delta^{18}O_{H2O}$ (‰)*
O3	8/17/06	4	7.7	6.0	7.9	-103	-11.4
	9/8/06	6	6.8			-103	-11.0
	9/22/06	6	4.9			-99	-11.3
	10/4/06	6	5.2			-99	-11.2
	10/20/06	4	4.1	6.1	5.3	-99	-10.1
	11/2/06	4	4.7			-100	-11.4
	12/9/06	2	4.1			-103	-10.7
	1/22/07	2	3.6			-99	-11.5
	2/15/07	4	3.8			-100	-11.5
	3/24/07	1	2.6			-106	-12.7
	5/5/07	1	7.7			-100	-11.7
	6/16/07	3	9.4			-101	-11.7
	7/15/07	8	9.5			-101	-11.9
	8/18/07	2	6.3			-101	-11.8
	10/5/07	1	5.4			-100	-11.4
	11/17/07	1	5.6			-98	-11.3
	12/29/07	1	5.9			-101	-11.5
	1/27/08	1	5.7			-106	-11.4
	3/8/08	1	5.7			-106	-11.5
	4/24/08	1	6.9			-108	-12.3
Hwy	8/2/06		4.6	6.1	1.5	-104	-11.2
	8/17/06		4.3			-102	-11.5
	9/8/06		4.5			-102	-11.2
	9/22/06		3.3			-100	-11.0
	10/5/06		3.2	6.1	-0.5	-98	-11.1
	10/20/06		2.2			-101	-10.1
	11/2/06		2.5			-98	-11.2
	12/9/06		2.3			-100	-10.9
	1/22/07		2.5			-99	-11.1
	2/15/07		2.9			-99	-11.5
	3/24/07		3.2			-99	-11.4
	5/5/07		3.0			-101	-11.4
	6/16/07		3.6			-99	-11.4
	7/15/07		3.4			-99	-11.5
	8/18/07		3.4			-100	-11.6
	10/5/07		3.9			-101	-11.6
	11/17/07		4.6			-99	-11.3
	12/29/07		4.2			-99	-11.4
	1/27/08		4.6			-104	-11.7
	3/8/08		4.1			-105	-11.2
	4/24/08		4.7			-106	-12.0